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Economic Geology

and the

Bulletin of the Society of Economic Geologists

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ECONOMIC GEOLOGY

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THE SOLUBILITY AND TRANSFER OF SILICA AND OTHER NON-VOLATILES IN STEAM.[1]

THOMAS E. GILLINGHAM.

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[1] This work started in 1940 under the S. F. Emmons Memorial Fellowship, was interrupted by the war, and was completed in 1946, when the results were submitted as a Ph.D. thesis to the faculty of the University of Minnesota. An abstract of the results was presented before the Geological Society of America at the Chicago Meeting in December, 1946.

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ABSTRACT.

Recent experiments show that several non-volatile substances are appreciably soluble in supercritical steam at pressures above 200 kg/cm². Steam at 450° C and 304 kg/cm² dissolves 240 ppm of silica from gel. Higher pressures caused by rise in temperature increase solubility. Also, at constant temperature solubility increases with rise in pressure.

By placing various oxides or carbonates in platinum crucibles near the top of a steel bomb and water and silica gel in the bottom, silica is transferred through steam at a rate which increases with pressure and which is dependent upon the "reaction potential" between silica and the substances in the crucibles.

Kaliophilite, muscovite, pyrophyllite, wollastonite, serpentine, forsterite, brucite, and talc were synthesized. Wollastonite was formed by transfer of silica to Iceland spar. Silica and magnesium oxide formed serpentine and brucite when the temperature was below about 435° C and forsterite and brucite when the temperature was higher. At 522° C and about 650 kg/cm² talc and forsterite were obtained. In experiments involving temperatures above 450° C the silica gel frequently altered to euhedral crystals of quartz. If this happened, transfer would be very much slower on account of a lowered reaction potential.

It may be concluded that steam at pressures above 300 kg/cm² is a powerful solvent of nonvolatiles such as silica. Pressure may be almost as important as temperature in the formation of mineral deposits by emanations.

INTRODUCTION

MANY geologists believe that the fluid responsible for most "hydrothermal" metamorphism and for many hypogene mineral deposits is a *dilute* aqueous solution derived from a magma. As to the relative importance of the gas phase of this fluid, there is no concensus, mainly because of the scarcity of data on the solubilities of non-volatile substances in gases.

If we premise that the mobile agent *is* predominantly water substance, and that the temperature of the agent and the pressures may be supercritical, then any evidence for gaseous solubility should be considered in formulating a theory of ore deposition.

What is a Gas?—The distinctions between the three states of matter, as explained by the kinetic theory, are too well known to require detailed restatement here. Suffice to say, this theory holds that the particles of matter in a solid or in a liquid are more or less bound together, whereas in the gaseous state the molecular particles move with relative freedom.

Provided the heat energy of a substance is maintained above a certain critical level, definite for each substance, that substance *must* exist as gas,

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no matter what pressure bears upon it. Increased pressure of course increases the density of the gas,[2] and as Hannay (2)[3] stated:

> We may compress a gas (above the critical temperature) to a less volume than it might occupy as a liquid and it will still remain gaseous.

This concept has been re-emphasized recently by Kennedy (3).

Static head of rock alone would produce a pressure of 1000 kg/cm² at a depth of about 4 kilometers.[4] But the strength of the superincumbent rock, obviously difficult to assess, may permit such pressure to obtain, over a small area, considerably closer to the surface.

The gas that the geologist must consider is a dense gas, very much like its corresponding liquid perhaps, except that the molecules are not in liquid association, and possess, therefore, greater mobility.

Solvent Ability of the Gaseous State.—The subject of the solubility of solids in gases has received relatively little attention from physical chemists, yet there is considerable evidence, both natural and experimental, that gases are effective solvents of non-volatile solids.

Knopf (5) in discussing the genesis of mineral deposits by supercritical aqueous solutions referred to the early work of Hannay and Hogarth who, between 1879 and 1882, published a series of papers on gaseous solubility and critical phenomena. Their work and subsequent researches by Centznerszwer and his collaborators have been summarized by Ingerson (6). Hannay (7) concluded that:

> . . . the liquid condition of fluids has very little to do with their solvent power, but only indicates molecular closeness. Should this closeness be attained by external pressure instead of internal attraction the result is that the same or even greater solvent power is attained; greater because of the greater activity of the molecules so compressed.

Limitations of the Critical State.—The presence of a non-volatile solute in an aqueous solution raises the critical temperature of the solution above that of pure water in proportion to the concentration of the solute. Morey and Ingerson (8) have discussed the fundamental relations of solubility to critical phenomena and have shown that a concentrated aqueous solution may not have a critical level. On the other hand, Schröer (9) found, for example, that a maximum 5 percent (0.810 mol per liter) solution of NaCl had a critical temperature 36.5° C higher than the critical temperature of pure water. Khitarov (10) obtained results that indicate the same order of critical temperature elevation for various dilute solutions. If the aqueous mobile agent contains no more than, say, 15 per cent non-volatile solutes, it is probable that the critical temperature will be below 500° C.

Present Work.—This paper presents the results of about one hundred experiments, made to determine what quantities of silica can be transferred through steam and what minerals form by the reactions of various compounds with steam-borne silica. Some data on actual solubilities of non-volatile sub-

[2] Steam at 400° C and about 2,000 kg/cm² pressure is much denser than liquid water just below its critical point and about as dense as water at 270° C (1).

[3] Numbers in parentheses refer to Bibliography at end of paper.

[4] Assuming the average density of rock to be 2.75 (4, p. 157).

stances in steam were obtained. The experiments were performed at moderately high pressures and at temperatures ranging from 350° C to 575° C. The water component of the system was always predominant; consequently, the gas state was involved in most cases.

It is hoped that the results will be of interest to geologists concerned with the problem of ore genesis, and that further experimental work along the same lines will be undertaken by other investigators.

The problem was suggested by Dr. John W. Gruner, whose continued interest and indispensable advice are gratefully acknowledged. The writer is indebted also to Dr. R. B. Ellestad, Dr. F. F. Grout, Mr. Lynn Gardiner, and Mr. John Phelan for many helpful suggestions. Mr. J. L. Ramisch of the Geophysical Laboratory of the Carnegie Institute of Washington kindly explained certain experimental procedures.

Funds for the research were provided by separate fellowship grants from the University of Minnesota and from the Samuel Franklin Emmons Memorial Fellowship Committee of the Society of Economic Geologists. The writer wishes to express his deep gratitude to these sources of aid.

DEFINITIONS.

The authority for most of the following definitions is Glasstone (11).

Critical Density.—The density of a substance at its critical temperature and critical pressure.

Critical Isotherm.—The pressure-volume curve of a substance for its critical temperature.

Critical Pressure.—That pressure required to cause liquefaction at the critical temperature. It is the maximum vapor pressure that a liquid can exert.

Critical Temperature.—That temperature above which a gas cannot be liquefied, no matter what the pressure.

Critical Volume.—The volume occupied by one mole of a substance at the critical temperature and critical pressure.

Degree of Filling.—The portion of the volume of a given container occupied by a quantity of a liquid at given conditions (writer's definition). For example, 10 cc of water at room temperature and atmospheric pressure will occupy ⅕ or 0.20 of the volume of a 50 cc container. The value 0.20 is the degree of filling for this case. The values in this paper were calculated for room temperature and atmospheric pressure.

Gas.—The state of maximum freedom of molecules of a substance. As used in this paper the term applies only to the gaseous state *above* the critical temperature, in contrast to the term "vapor," *q.v.*

Gaseous State.—The state of matter, comprising both the gas and the vapor, in which the molecules are not attached to each other. (This is a somewhat arbitrary definition.)

Specific Volume.—The volume occupied by one unit weight of a substance. It is the reciprocal of density and is expressed in cubic centimeters per gram.

Steam.—Water in the gaseous state.

Vapor.—The state of a substance in which the molecules have attained virtual freedom *below* the critical temperature, *i.e.*, the gaseous state below the critical temperature. A vapor can be condensed to a liquid by pressure alone. The distinction between a gas and a vapor, while perhaps academic, is nevertheless useful, and is accordingly recognized by physical chemists.

Vapor Pressure.—The pressure exerted at a particular temperature by a vapor which is in equilibrium with the liquid at that temperature. Strictly, this term should be "saturation vapor pressure," but this is implied by the stipulation "in equilibrium with the liquid."

APPARATUS.

The experiments were performed in small steel bombs which were heated in compact electric furnaces. Large bombs have no advantages for this type of experiment.

Bombs and Accessories.—Two types of bombs were used. The first, described by Foreman (12),[5] has an effective volume of 58 cc. It has been used successfully in hydrothermal experiments at Minnesota but is not recommended for experiments involving supercritical conditions. The second type (Fig. 1) is the writer's modification of a design by Morey and Ingerson (13). The modifications include the double threads, for greater ease in opening, and the semi-conical shaping of the lower end of the plunger, to provide a more concentrated "cold point" for the condensing experiments. This second type bomb, which has an effective volume of about 34 cc, served satisfactorily.

Accessories included 7 cc platinum crucibles, platinum wires for supporting the crucibles in the bombs, and a special fitting for condensing experiments. The ideal lubricant for the bomb threads is a moderately thick mixture of fine flake graphite and glycerine.[6]

Electric Furnaces and Temperature Controls.—The resistance-type furnace, with a delicate, "built-in" temperature-control mechanism, has been described by Norton (14). With constant room temperature and with careful adjustment, the temperature of the furnace will not fluctuate more than one or two degrees over long periods.

Temperatures were measured by means of a chrome-alumel thermocouple. The hot terminal was inserted in the condenser well of the bomb and the cold terminal was attached to a Leeds and Northrup potentiometer.

EXPERIMENTAL METHODS AND TECHNIQUES.

The experiments were of two types: first, condensing experiments, designed to produce data on the solubilities of substances in steam; and second, transfer experiments, by which rates of transfer of substances through steam were obtained.

Method for Condensing Experiments.—A quantity of the solid substance whose solubility was to be determined and 5 cc of distilled water were poured

[5] In present experiments, the gold linings described by Foreman were not used.

[6] Suggested by J. L. Ramisch, personal communication, 1940.

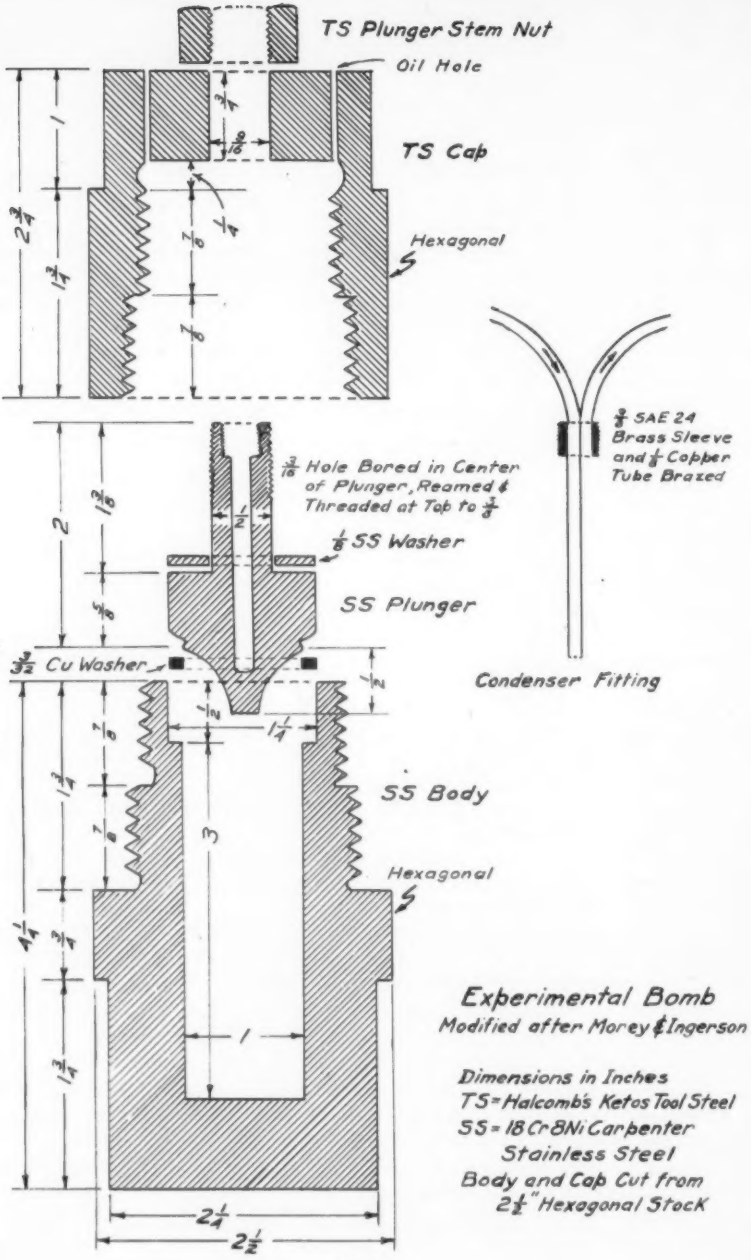

TS Plunger Stem Nut
Oil Hole
TS Cap
Hexagonal
3/16 Hole Bored in Center of Plunger, Reamed & Threaded at Top to 3/8
1/8 SS Washer
SS Plunger
3/32 Cu Washer
SS Body
Hexagonal
1/8 SAE 24 Brass Sleeve and 1/8 Copper Tube Brazed
Condenser Fitting
Experimental Bomb
Modified after Morey & Ingerson
Dimensions in Inches
TS = Halcomb's Ketos Tool Steel
SS = 18 Cr 8 Ni Carpenter Stainless Steel
Body and Cap Cut from 2 1/2" Hexagonal Stock

FIG. 1.

into the bottom of a bomb. A clean, dry, uncovered 7 cc platinum crucible on a coiled platinum wire support was then placed in the bomb so that the crucible rested as near the top as possible. Carbon dioxide gas was introduced through a fine glass nozzle to displace the air. Finally, the bomb was sealed by inserting the copper washer and plunger and tightening the cap. The bomb thus charged was placed in a cold furnace and the temperature raised as quickly as possible.

At the end of the run the hot bomb was clamped in a vise, the special condenser fitting screwed into the plunger, and cold water introduced through the special fitting into the condenser well. The effect of the water impinging on the interior of the plunger was to condense the steam in the bomb into liquid which dropped into the crucible. After about five minutes of the condensing action, the bomb was immersed in a cold water bath to prevent evaporation of the condensate.[7]

The crucible and its contents were carefully removed from the bomb and weighed. The liquid was then evaporated off and the residue, if any, was brought to complete dryness over a low flame, cooled, weighed, and tested chemically. If silica was expected, the residue was treated with HF and any loss in weight noted.

It was assumed that any solid substance which was found in the crucible at the completion of the experiment, but which at the start was only in the bottom of the bomb, would have been in solution in the quantity of steam represented by the volume of condensate recovered.

Method for Transfer Experiments.—In these experiments the condenser was not used. Rather, a solid substance, generally silica gel, and distilled water were placed together in the bottom of a bomb, and a platinum crucible containing a weighed amount of a solid "collector" was placed on the platinum wire support near the top of the bomb. Carbon dioxide was used to displace the air and the bomb was otherwise made ready for heating as described in the previous section.

After a run of a definite number of hours, the bomb was quickly cooled by immersion in cold water. On opening the bomb, the crucible contents were found in nearly all cases to be quite dry.

Since in the silica experiments it was necessary to ascertain both the quantity of silica transferred and identity of the product, the material in the crucible after weighing was separated into two parts, the larger for chemical analysis, the smaller for X-ray determination. The silica finally determined from the larger sample was corrected proportionately to include the silica in the sample taken for X-ray. Silica was determined gravimetrically.

Identification of Products.—For identification of small quantities of the very fine-grained crucible products, X-ray powder patterns were used, supplemented in some cases by optical methods. Precision cameras of 57.3 mm radii and unfiltered iron radiation gave excellent patterns that could be compared readily with known ones.

[7] The condensing method, following essentially this procedure, was devised by Drs. Morey and Ingerson and was outlined to the writer by Mr. J. L. Ramisch, personal communication, 1940.

Substances Used in the Experiments.—Distilled water and the following minerals or chemicals of analytical grade were used: aluminum hydroxide, which gave the X-ray pattern of bayerite; barium chloride hydrate, $BaCl_2 \cdot 2H_2O$; calcium carbonate (Iceland spar), calcium oxide, magnesium oxide; microcline, $KAlSi_3O_8$; potassium carbonate, and sodium carbonate. The silica gel was supplied in pellet form by the Silica Gel Corporation, Baltimore, Maryland. The pellets were crushed in a steel mortar and screened to $-20+30$ mesh.

DETERMINATION OF PRESSURE.

The bombs were not fitted with pressure gauges; consequently pressures had to be calculated from volume, degree of filling, and temperature. Since the solutions used in the experiments were very dilute, the recorded pressures are those of pure water substance [8] plus a correction of 2 kg/cm² for the partial pressure of the carbon dioxide used to displace the air.[9]

At high pressures and temperatures the ideal gas law does not apply precisely, nor do any of the equations of state yield accurate results over any considerable range (15). The most accurate values are obtainable from empirical compilations such as steam tables.

For this paper, the kilogram per square centimeter (kg/cm²) has been adopted as being most easily applied to geologic problems.[10]

In calculating pressures, there are three possible cases. In the first case, which applies only below the critical temperature of water, both liquid and vapor exist; the pressure is then the saturation vapor pressure of steam. In the second case, the vapor alone exists as superheated or dilated steam below the critical temperature; the pressure is then obtained from steam tables (16). In the third case, steam exists as a gas, *i.e.*, above the critical temperature, and the pressure can be obtained from either steam tables or from the isothermal curves for water after van Nieuwenburg and Blumendal (17) shown in Fig. 2. It is believed that the calculated pressures are correct to within 5 kg/cm².

SOLUBILITIES OF NON-VOLATILE SUBSTANCES IN STEAM.

Previous Work.—Relatively few data on gaseous solubility exist. Researches on the solubility of the various forms of silica by Lenher and Merrill (18), Gruner (19), Hitchen (20), and Kennedy (3) gave results which show rather conclusively that the solubility of silica *in liquid water* increases with temperature to a point close to the critical point. Comparison of these data shows that quartz is less soluble than silica glass and silica glass is less

[8] Goransen's (1) values for the critical constants of water:

Critical temperature, t_c	374.11° C
Critical pressure, p_c	221.06 bars or 225.42 kg/cm²
Critical volume, v_c	3.1975 cc/gram
Critical density, d_c	0.313 gram/cc

[9] The correction for partial pressure of CO_2 represents an average for the temperature range of the experiments.

[10] 1 kg/cm² = 0.980665 bar = 0.967842 atm = 14.2234 lbs/in².

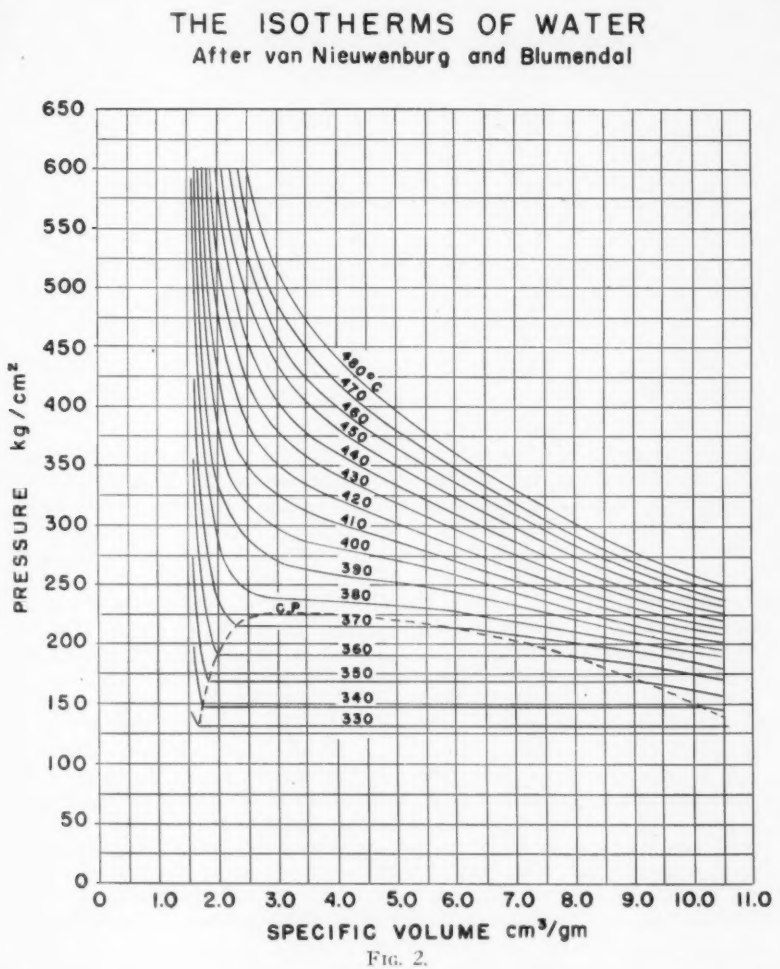


FIG. 2.

soluble than amorphous silica. But there is a possibility, pointed out by Frondel (21) that colloidal dispersion may account for a part of the reported "solubilities," so that true solubilities may be somewhat lower.

The first quantitative data on the solubilities of the forms of silica *in steam* were those of Syromyatnikov (22) and of van Nieuwenburg and van Zon (23). Later "exploratory" runs by Kennedy (3) yielded some data. Comparable results of these investigators are shown in Table 1.

TABLE 1.

SOLUBILITIES OF SILICA GLASS, DIATOMITE AND QUARTZ IN SUPERCRITICAL STEAM

Investigator	Substance	Temp., °C	Press., kg/cm²	Solubility in Parts per 10^6 Parts Water
Kennedy	Silica Glass	377	310	1700
		399	310	1400*
		418	310	950
Syromyatnikov	Diatomite	400	313	750*
Van Nieuwenburg and van Zon	Quartz	380	295	434
		380	(310)	(491)
		380	330	566
		400	293	200
		400	(310)	(324)*
		400	325	434

Note: The figures in parentheses were obtained by straight line interpolation to give more comparable data.

* The starred figures are comparable.

The paper by van Nieuwenburg and van Zon merits a brief summary. The two Dutch scientists performed a large number of experiments and obtained "semiquantitative" data which they plotted as isothermal solubilities against pressure. They heated 0.100 gram portions of finely powdered quartz in a small crucible at the top of a 19 cc bomb, with sufficient water in the bottom of the bomb to give a desired pressure of steam at a certain temperature. The experiments ran for five hours after the temperature was reached, and it was claimed that equilibrium was always attained. Solubility was determined on the basis of the loss in weight of the quartz in the crucible. The results of the work, reproduced in Fig. 3, A and B, show an *increase* in solubility with a *decrease* in temperature at constant pressure, and an *increase* in solubility with an *increase* in pressure at constant temperature. The isotherms seem to converge at higher pressures, however, and the investigators concluded that solubility is not much increased by pressures above 600 kg/cm² and is lessened by increased temperature. Using data from these experiments with certain interpolations, the writer prepared the curves shown in Fig. 3 C. Solubility of quartz was plotted against temperature, and points of equal pressure were connected by isobars. The curves show that as pressure increases up to 500 kg/cm² the solubility is less and less affected by temperature differences. The 500 kg/cm² isobar is parallel to the abscissa; therefore, at this pressure the solubility is the same at all temperatures shown and is univariant.

The comparisons given in Table 1 indicate that the solubilities of silica glass, diatomite, and quartz in steam at about 400° C and 310 kg/cm² are 1400, 750, and 324 parts per million respectively. As would be expected, silica glass and diatomite show higher solubilities than quartz, but the discrepancy between Kennedy's result (1,400 ppm) for silica glass and Syromyatnikov's result (750 ppm) for diatomite is rather large and suggests a possible error in Kennedy's method.

SOLUBILITY OF QUARTZ IN STEAM

According to van Nieuwenburg and van Zon

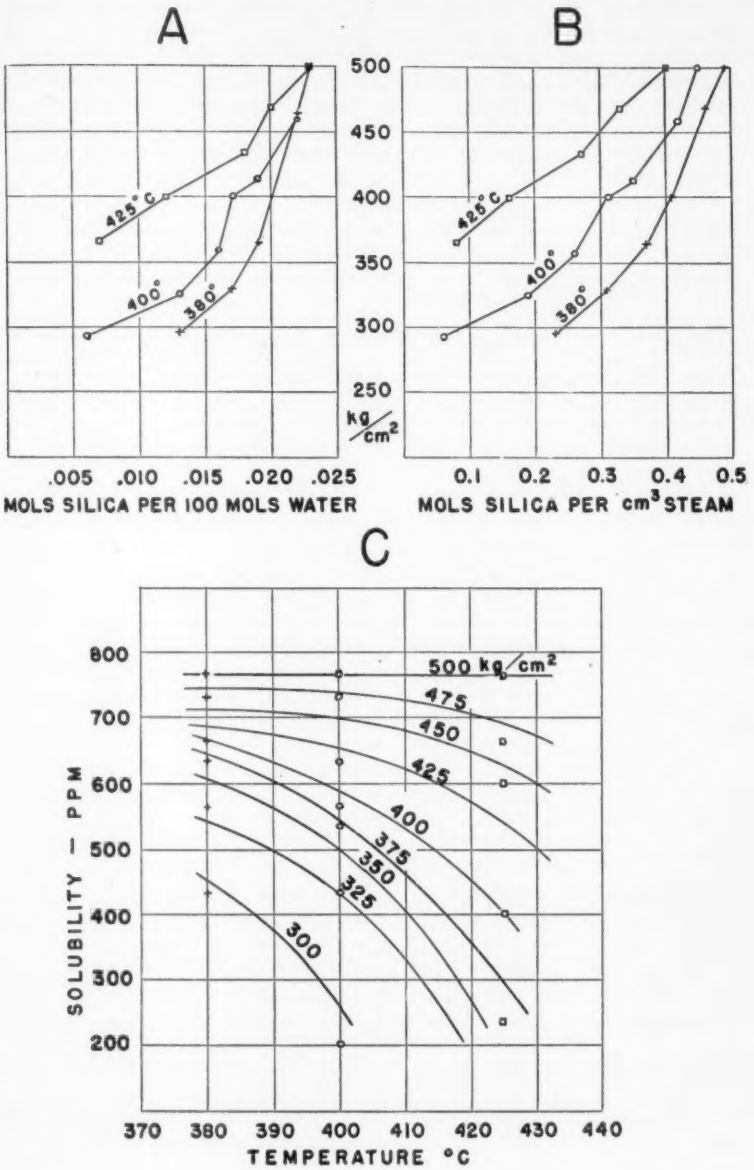


FIG. 3.

Experiments on the Solubility of Silica.[11]—Six experiments in this category were performed, using the condensing method described above. Substances used were silica gel or microcline. The data and the results of these experiments are given in Table 2. The solubilities were calculated from the ratios of the silica recovered in the crucible to the water recovered in the crucible. Variations in the amount of condensate were probably due to differences in the rate of cooling; in each case the balance of the water was found

TABLE 2.

THE SOLUBILITY OF SILICA GEL AND SILICA FROM MICROCLINE.

Amt. of water used ..... 5 cc
Degree of filling 0.147
Vapor pressure of CO_2 added ..... 2 kg/cm²
Volume of bomb ..... 34 cc

Exp. No.	Temp., °C	Pressure, kg/cm²	Time, Hrs.	Material Below, Grams	Water Recovered, cc	Silica in Crucible, Grams	Solubility—Parts Silica/10⁶ Parts Water
17	350	171	42	0.10 Silica Gel Powdered	3.61	none	—
18	370	212	77	0.10 Silica Gel Powdered	4.92	0.0004	80
3	450	304	17	0.20 Silica Gel Powdered	2.94	0.0007	240
4	450	304	46	0.26 Microcline Powdered	4.91	0.0006	120
5	450	304	115	0.26 Microcline Powdered	4.52	0.0013	290
6	450	304	114	0.57 Microcline Sized (.4 mm)	4.45	0.0004	90

in the bottom of the bomb. It is assumed that the silica recovered in the crucible was dissolved in the steam represented by the condensate in the crucible. The condensate in each experiment was quite clear.

No claim is made that equilibrium and, therefore, maximum solubility were attained in these six experiments. In the case of powdered microcline, the solubility seems to be roughly proportional to time. More important than time is the factor of particle size; thus powdered material, which presents a maximum surface to the solvent, shows a much greater solubility, other

[11] With respect to the experiments in which microcline was used, it should be stated that the dissolved silica was that obtained from the breakdown of the silicate in the steam environment.

factors being constant, than larger sized particles. Silica gel shows a higher solubility than the silica obtained from microcline.

In Exp. 17 both liquid and vapor were present and solubility in steam was apparently nil. In Exp. 18, although the temperature was below the critical, the degree of filling was insufficient to cause saturated vapor; therefore, no liquid was present at 370° C. Nevertheless the vapor was quite dense and some silica gel dissolved. Further experiments along this line may confirm the conclusion suggested by these two experiments—that silica gel is somewhat soluble in steam *below* the critical temperature provided the vapor is sufficiently dense and the temperature is relatively near the critical point. In several of the transfer experiments described below, silica was transferred below the critical temperature when liquid, as well as vapor, was present. This implies that the vapor need not be in direct contact with the solid to effect a silica content in the vapor. But in such cases the liquid probably retains most of the solute and the "solubility" in the vapor, while finite, may be exceedingly low; and, as in Exp. 17, not detectable by ordinary means. On the other hand, if the degree of filling is so low that all the liquid is converted to vapor before the critical temperature is reached, then most of the material dissolved in the liquid might be taken into solution in the vapor.

If all the variables—temperature, pressure, time, relative amounts and nature and fineness of the material—are considered, the results of the six experiments are consistent among themselves.

In Table 1 various determinations of solubility at 400° C and 310 kg/cm² were compared; and it was brought out in Fig. 3 that in the lower supercritical range the solubility of a given form of silica *decreases* with increased temperature, the pressure remaining constant, and *increases* with increased pressure, the temperature remaining constant. If we compare the solubilities of silica gel and diatomite, we should expect at the 450° C temperature and the 304 kg/cm² pressure of Exp. 3 a solubility lower than the 750 ppm reported by Syromyatnikov for 400° C and 310 kg/cm². The solubility of silica gel determined in Exp. 3 was 240 ppm or 510 ppm less than Syromyatnikov's result. This is a considerable decrease but is in the expected direction.

Experiments on the Solubility of Potassium Carbonate.—The solubility of potassium carbonate was studied in the experiments recorded in Table 3. As the normality of the solution used was 0.036, the small quantity of solute could not have raised the critical temperature of water notably.

The results indicate that a large percentage of the potassium carbonate soluble in liquid water is soluble also in steam. For temperatures much below the critical, as in Exps. 77 and 75, where both liquid and vapor existed, condensation must have entailed violent boiling of the liquid, so that mechanical spattering gave high results. In Exp. 74 the vapor was unsaturated and, therefore, liquid was not present. Hence, it is difficult to explain the fact that Exp. 74 gave a higher result than Exp. 70.

It is believed that the results of Exps. 70, 67, 64, covering the lower range of supercritical temperature, may represent fairly reliably the solubility at the respective conditions. These three results show a rise in solubility with rise in temperature-pressure.

TABLE 3.

THE SOLUBILITY OF ANHYDROUS POTASSIUM CARBONATE.

Amt. of K_2CO_3 used	0.0500 gram
Amt. of water used	5.0 cc
Conc. of K_2CO_3/gram H_2O	0.01 gram
Degree of filling	0.145
Vapor pressure of CO_2 added	2 kg/cm²
Volume of bomb	34.5 cc

Exp. No.	Temp., °C	Pressure, kg/cm²	Time, Hrs.	Liquid Recovered, Grams	K_2CO_3 Residue, Grams	Conc. K_2CO_3/ Gram Steam	% K_2CO_3 in Liquid Water Soluble in Steam
77	350	170	19	4.11	0.0094	0.0023	23
75	363	193	22	3.21	0.0151	0.0047	47
74	370	206	5½	3.39	0.0118	0.0035	35
70	385	225	5½	3.94	0.0118	0.0030	30
67	400	243	6	3.40	0.0178	0.0052	52
64	425	272	8	4.10	0.0284	0.0069	69

Experiments on the Solubility of Aluminum Hydroxide.—Two experiments were made to determine the solubility of bayerite, $Al_2O_3 \cdot 3H_2O$ or $Al(OH)_3$, in steam at 450° C. At atmospheric pressure bayerite loses two molecules of water at 300° C and the third molecule at 360° C. Its solubility at 20° C is 0.00015 parts per 100 parts of water. In each experiment 0.6 gram of the hydroxide and 5 cc of distilled water were placed in a 34 cc bomb. The degree of filling was 0.147 and the pressure developed at 450° C was about 304 kg/cm². One experiment ran for 44 hours; the other for 77 hours. No alumina residue was found in the crucible in either case, suggesting that bayerite, which is practically insoluble in liquid water, is also insoluble in steam at 450° C and 304 kg/cm².

Experiment on the Solubility of Barium Chloride.—The solubility of barium chloride hydrate, $BaCl_2 \cdot 2H_2O$, was tested in a single experiment. This salt loses its water molecules at 113° C and shows a water solubility at 20° C of 35.7 parts per 100, and at 100° C of 58.7 parts per 100. In the experiment 0.05 gram of barium chloride and 5 cc of distilled water were heated in a 34.5 cc bomb at 426° C under 273 kg/cm² pressure for 24 hours. The condensate weighed 4.67 grams. The residue after the evaporation weighed 0.0019 gram. Although no quantitative chemical analysis of the small residue was made, the result indicates that barium chloride is probably soluble in steam.

Experiment on the Solubility of Sodium Carbonate.—The solubility of anhydrous sodium carbonate in water at 0° C is 7.1 parts per 100, and at 100° C is 45.5 parts per 100. In the experiment 0.05 gram of the salt and 5 cc of distilled water were heated in a 34.5 cc bomb at 425° C and 272 kg/cm² pressure for 27 hours. Practically no residue was left from the condensate and this residue did not give a sodium reaction. This single result indicates that sodium carbonate may be insoluble in steam at 425° C and 272 kg/cm² pressure.

TRANSFER OF SILICA AND OTHER NON-VOLATILES IN STEAM.

Previous Work.—Jeffreys (24) noted the corrosion of siliceous bricks by high-temperature steam and the deposition of siliceous crusts on stoneware placed in the cooler parts of the furnace. Similar notes have been made by many observers, but the records have been almost entirely qualitative.

The first systematic investigation of the ability of a gas to transfer a solid seems to have been that of van Nieuwenburg and Blumendal (25), performed in autoclaves, similar to the bombs used in the present investigation. Their work has been summarized by Morey and Ingerson (8). In their experiments, amorphous silica, quartz, cristobalite, and tridymite were tested separately. The transfer was calculated from the loss of weight of silica from one crucible and the gain in weight of a "collector," zinc oxide, in another crucible. The authors noted that the amount of transfer increased with the fineness of the silica particles.

TABLE 4.

SYNTHESES OF SILICATES BY SILICA TRANSFER BY VAN NIEUWENBURG AND BLUMENDAL.

Oxide Used	Temp., °C	Press., Atms.	Time, Hrs.	Minerals Produced
(a) CaO	365	200	48	Beta wollastonite and calcite
(b) MgO	395	300	72	Antigorite and clinoenstatite
(c) CaO	365	200 H_2O 100 CO_2	48	Calcite
(d) MgO	365	200 H_2O 100 CO_2	48	Magnesite and antigorite

Morey (26) questioned the work of the Dutch investigators, pointing out that the degree of filling used would entail the flooding of the crucibles with liquid water before the critical temperature was reached, and that, consequently, much of the transfer would have taken place through the liquid medium. Morey repeated the experiments with considerably lower degrees of filling and found that only 0.0001 to 0.0004 grams of silica were transferred during runs of from 4 to 25 days.

In subsequent experiments van Nieuwenburg and Blumendal (27) directed their attention only to the syntheses of various minerals by silica transfer, using the method of their earlier experiments, but employing a series of different oxides as "collectors." Apparently no measurements were made of the quantities of silica transferred; hence, the results are qualitative only. Morey and Ingerson (8) have tabulated the results of this work. The selected data shown in Table 4 are of particular interest here. It should be noted that Morey's objections mentioned above apply to result (b) of Table 4, where 300 atmospheres pressure at 395° C implies flooding of the crucible with liquid water.

Greig, Merwin, and Shepherd (28) have shown by experiment that cristobalite could be formed by "volatile" transfer of silica from a series of

rocks ranging in composition from obsidian to basalt. The temperatures ranged from 600° C to 1200° C. The experiments were performed in evacuated silica tubes. It was concluded that water alone could effect transfer at "an important rate," although no quantitative measurements were made.

Syromyatnikov (22) synthesized serpentine by transferring silica through steam to a magnesium hydroxide "collector." His results are "quantitative," but, unfortunately, the quantities of materials used are not given, nor is the method of identifying the serpentine indicated.

There is evidence that substances other than silica are transferable through steam. Ingerson and Morey (29) report that iron was deposited on a thermocouple which was suspended in a bomb in such a way that the iron, in the form of Fe, Fe_2O_3, or $Fe(OH)_3$, could have been extracted from the metal in the bomb wall and carried to the thermocouple only through steam free from halogens.

Morey (30) reported the formation of sillimanite, rutile, corundum, quartz, and amorphous silica on the thermocouple tube in a bomb which contained steam under a pressure of about 3,000 psi (210 kg/cm²). The silica, alumina, and titania were dissolved from refractories in the bomb by the steam at about 1000° C and deposited on the thermocouple leads and on surfaces where the temperature in places was less than 1000° C.

Scope of Present Transfer Experiments.—Applications of the transfer technique described above included two preliminary experiments and four groups of experiments with different "collectors": sodium carbonate, calcium carbonate and calcium oxide, aluminum hydroxide, and magnesium oxide. In the majority of the experiments, the substance transferred was silica only.

The residual liquids from the transfer experiments were tested with litmus paper, and, unless otherwise noted, were neutral or very slightly acid. The reactions took place therefore in essentially neutral environment—a fact of considerable interest from the geological viewpoint.

The results of most of the transfer experiments are plotted as curves which may be termed "transfer curves." A single curve shows the quantities of silica transferred at different temperatures when the degree of bomb filling and the duration of the runs are constants. Since pressure increases with temperature, the plot is one of composite temperature-pressure against quantity transferred in a certain period of time.[12]

Preliminary Experiment No. 10—Attempt to Synthesize Orthoclase.—A mixture of potassium carbonate and aluminum hydroxide, in the proportion required to meet the $K_2O:Al_2O_3$ ratio in orthoclase, was used as the "collector" in the platinum crucible. Distilled water sufficient to create a steam pressure of 302 kg/cm² at 450° C, and 0.2000 gram of silica gel were placed in the bottom of a 34 cc bomb. After a run of 330 hours it was found that the orthosilicate, kaliophilite, $KAlSiO_4$, had formed in the crucible, showing that silica had been transferred to the "collector" through the steam. The

[12] Since time is constant, a curve may be considered as showing the variations in the *rate* of transfer, that is, in the quantity transferred per "unit" of time, where the "unit" is the duration of the run. From the results tabulated, an average day-rate or hour-rate could be obtained by simple arithmetic. For experiments in which different durations of runs were involved, this approach would be advisable.

kaliophilite gave an excellent X-ray pattern which agreed with the pattern obtained from a sample of pure, synthetic kaliophilite furnished by Dr. G. W. Morey. The silica gel in the bottom of the bomb inverted to quartz during this long run.

The reaction of which kaliophilite was the end product required one-third the amount of silica required for orthoclase. Kaliophilite would be expected as the first product if silica were added gradually to the potash-alumina mixture. It is possible that the disilicate, leucite, $KAl(SiO_3)_2$, would have formed as the second stage in a longer run.

Preliminary Experiment No. 19—Synthesis of Muscovite.—The purpose of this experiment was to determine the effect of high-pressure steam on microcline and to see if any of the components of microcline are transferred through steam to a "collector." Five cc of distilled water and 0.15 gram of crushed microcline were placed in a crucible in the bottom of a 34 cc bomb, and 0.0360 gram of bayerite was placed in the upper crucible. The temperature was held at 575° C for 31 days; the pressure was about 440 kg/cm².

After this exceptionally long run, the materials in both crucibles were X-rayed and examined microscopically but were not analyzed. The products in the upper crucible were muscovite and another substance which could not be identified. Under the microscope the muscovite showed the fine, scaly, aggregated form and the optical properties of sericite and appeared to be the dominant product. The second substance, which gave several lines among the muscovite lines in the X-ray pattern, was optically isotropic with an index of refraction less than muscovite.

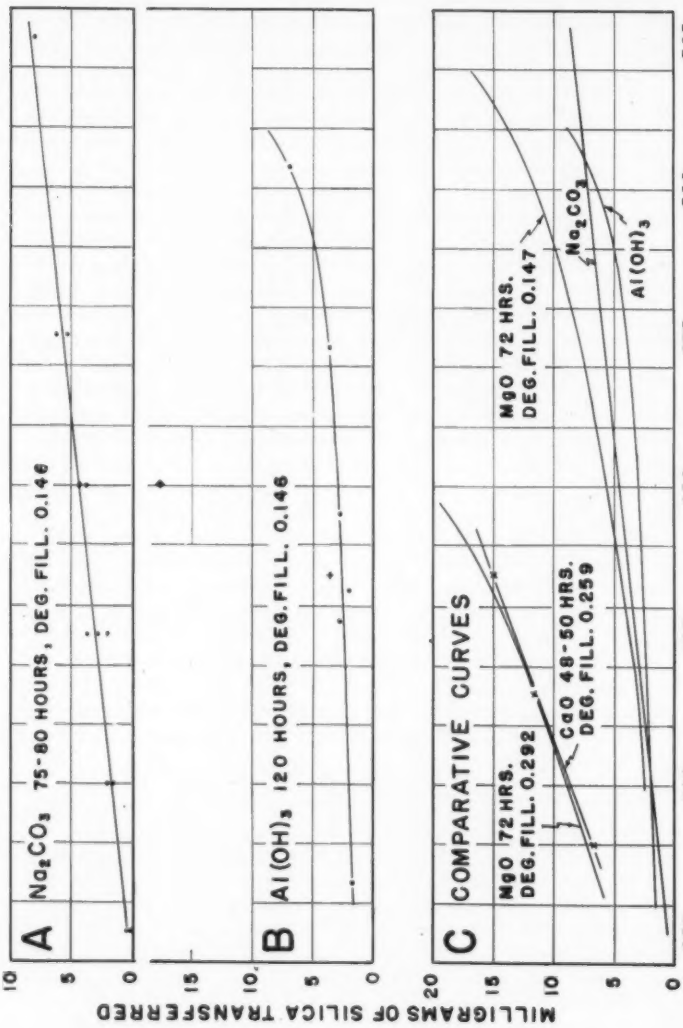
Strangely enough the residual fragments in the bottom crucible gave the X-ray pattern of microcline only, and under the microscope or binoculars showed no detectable alteration. However, a very thin white coating covered the walls of the bottom crucible when the residual water was evaporated; this may have been material that dissolved from the microcline but was not transferred to the "collector."

To form muscovite in the upper crucible, both potash and silica had to be transferred from the microcline through steam. The reaction was:

$$\underset{\text{From Bayerite}}{3Al_2O_3} + \underset{\text{From Microcline}}{K_2O} + 6SiO_2 + 2H_2O \rightarrow \underset{\text{Muscovite}}{2KAl_3Si_3O_{10}(OH)_2}$$

The temperature of the experiment (575° C) was 50° higher than the highest temperature for muscovite synthesis previously reported (31). The fact that the environment in this experiment was essentially neutral corroborates Gruner's observation that sericite forms in slightly basic to acid solutions when the proportion of potash is not too high. Exp. 10, described above, shows that kaliophilite forms in neutral environment when excess potash is present and silica is scarce.

Transfer of Silica to Calcite and to Calcium Oxide.—When magma intrudes a limestone, lime and carbon dioxide may be abstracted from the limestone and silica and other substances introduced from the magma. After agreeing that heavy metals may be introduced as halides, Lindgren (32,



TRANSFER OF SILICA TO VARIOUS COLLECTORS

FIG. 4.

p. 710) says: "The mode of transfer of silica from the intrusive to the limestone is a problem not yet fully solved."

At atmospheric pressure calcite decomposes into lime and carbon dioxide at about 885° C. Although it is not always clear what happens to the carbon dioxide in contact deposits, there is abundant evidence that silica reacts with lime to form wollastonite. Wollastonite has been synthesized at temperatures from 210° to 425° C, and also at red heat (8). Van Nieuwenburg and Blumendal (27) synthesized the mineral at 365° C by transfer of silica to calcium oxide, presumably through steam. There is no record of synthesis by transfer to calcite, as would be demanded in nature.

In Exp. 16, 0.07 gram of crushed Iceland spar was used as the "collector." Five cc of distilled water and 0.12 gram of silica gel were placed in the bottom of a 34 cc bomb. The temperature was held at 405° C for 115 hours; the pressure was about 252 kg/cm². Analysis of the product showed that 0.0049 gram of silica had been taken up by the "collector," and an X-ray pattern of the product showed, in addition to the strong lines of calcite, two of the strongest lines of wollastonite. Under the microscope some of the cleavage fragments of the calcite appeared to be corroded along the edges where groups of tiny crystals of wollastonite had developed. Under the binoculars, the wollastonite appeared as a white coating on the rhombs of calcite. This experiment demonstrates the ability of steam-borne silica to convert calcite to wollastonite.

Six experiments with calcium oxide as the "collector" were run at temperatures varying from 400° C to 465° C. The data and results are shown in Table 5 and, in part, in Fig. 4 C. The results for degree of filling 0.259

TABLE 5.

TRANSFER OF SILICA TO CALCIUM OXIDE.

Amt. of CaO in crucible..... 0.1000 gram
Amt. of silica gel used..... 0.50 gram
Vapor pressure of CO_2 added..... 2 kg/cm²
Volume of bomb..... 58 cc

Exp. No.	Temp., °C	Time, Hrs.	Water, cc	Degree of Filling	Pressure, kg/cm²	Silica Transferred, Grams	Crucible Product
63	400	48	15	0.259	283	0.0069	No X-ray
71	425	50	15	0.259	336	0.0116	Calcite and little wollastonite
60	445	48	15	0.259	378	0.0150	Wollastonite crystals and calcite
56	465	111	15	0.259	416	0.0303	Wollastonite and very little calcite
37	400	48	20	0.345	300	0.0257	Calcite and little wollastonite
39	425	48	20	0.345	373	0.0218	Calcite and little wollastonite

show increased transfer with increased temperature and with increased time. It is interesting to note the approximate concordance of the curve based on Exps. 63, 71, and 60 for calcium oxide with the portion of the magnesium oxide curve for slightly higher degree of filling (Fig. 4 C). The slopes of the two curves are almost identical, although certain data are not exactly comparable. The coincidence tends to substantiate in a general way the observation that for degrees of filling between 0.25 and 0.30 the increase

in transfer rate with rise in temperature is considerably greater than for degrees of filling below 0.15.

Exp. 56 ran for 111 hours at 465° C and the quantity of silica transferred was about double that transferred in 48 hours at 445° C. If this result were plotted in Fig. 4 C, the point would lie considerably above the projection of the CaO curve, and would thus show the effect of the additional time.

Exps. 37 and 39, with degree of filling 0.345, gave anomalous results, for they show decreased transfer with increased pressure and temperature. Since only two experiments were performed at this higher degree of filling, the results are not well established and have not been plotted.

The products of the six experiments were calcite and wollastonite. The calcite formed by reaction of the lime with the carbon dioxide used to displace the air; the wollastonite developed by reaction of the lime with silica transferred through steam. Calculations show that even in Exp. 56, when 0.0303 gram of silica was transferred, the quantities of silica and carbon dioxide available for reaction with the CaO were insufficient to convert all the CaO to calcite or wollastonite. But the X-ray patterns show no lines other than those of calcite and wollastonite; hence, it is not known in what form the excess CaO existed in the product.

These experiments demonstrate that wollastonite can form by silica transfer at temperatures at least as high as 465° C, *i.e.*, 40° higher than previously reported for comparable conditions.

Transfer of Silica to Sodium Carbonate.—The data and results of the experiments in which sodium carbonate was used as the "collector" are shown in Table 6 and in Fig. 4 A. With constant degree of filling, in runs of between 75 and 80 hours duration, the quantity of silica transferred to

TABLE, 6.

TRANSFER OF SILICA TO SODIUM CARBONATE.

Amt. of Na_2CO_3 in crucible ..... 0.0817 gram
Amt. of silica gel used ..... 0.2000 gram
Amt. of water used ..... 5.0 cc
Average degree of filling 0.146

Exp. No.	Temp., °C	Press., kg/cm²	Time, Hrs.	SiO_2 Transferred, Grams
27	375	214	76	0.0003
28	375	214	75	0.0004
34	400	247	76	0.0017
40	400	247	76	0.0021
29	425	276	76	0.0019
23	425	276	80	0.0027
32	425	276	78	0.0033
26	450	303	76	0.0039
24	450	303	76	0.0043
35	475	330	77	0.0052
33	475	330	76	0.0064
44	500	348	76	0.0074
43	525	385	76	0.0078

Note: The average degree of filling represents the average for the two bombs, *i.e.*, 0.145 for the 34.5 cc bomb and 0.147 for the 34 cc bomb. Since the difference in bomb volumes seemed to make no difference in the results, an average degree of filling was assumed.

sodium carbonate increased with temperature. Since pressure rises with temperature, it is not possible to determine from a single degree of filling curve the relation of transfer to either temperature alone or pressure alone. The slope of the transfer curve is constant from 375° C to 525° C, but since the 500° and 525° points were not checked, the portion of the curve above 475° may be in error.

The crucible products were examined optically and were analyzed for silica, but were not X-rayed. They were not identified. In several experiments aggregates of tiny, elongated, colorless crystals formed. One crystal from Exp. 24 measured 3 mm in length. Optically it was biaxial negative, with parallel extinction, low birefringence, and indices between 1.500 and 1.507. These crystals were probably one of the sodium silicates. They were insoluble in water.

A complete set of X-ray patterns were obtained from the residues of the silica gel in the bottom of the bomb. In every experiment the silica gel had altered to cristobalite.

Transfer of Silica to Aluminum Hydroxide.—Experiments with bayerite, the low-temperature crystalline trihydrate of alumina, $Al(OH)_3$, yielded the results shown in Table 7 and Fig. 4 B. Except in Exps. 9 and 15, the crucible was charged with 0.1000 gram of bayerite. Several experiments ran for 120 hours, and one each for 84, 144, and 333 hours. As in the sodium carbonate runs, the results show increased transfer with rise in temperature. If the curve is drawn through point 46 instead of point 47, an increasing slope at temperatures above 475° C is indicated.

Exps. 59 and 9, which ran for 144 hours and 333 hours respectively, yielded results which suggest that the amount transferred increases with time. The transfer for 144 hours in Exp. 59 gave a point 35 percent above the curve; the transfer for 333 hours in Exp. 9 gave a point 600 percent

TABLE 7.

TRANSFER OF SILICA TO ALUMINUM HYDROXIDE.

Amt. of silica gel used	0.2000 gram
Amt. of water used	5.0 cc
Average degree of filling	0.146
Vapor pressure of CO_2 added	2 kg/cm²
Volume of bombs	34 or 34.5 cc

Exp. No.	Temp., °C	Pressure, kg/cm²	Time, Hrs.	Bayerite in Crucible, Grams	SiO_2 Transferred, Grams	Crucible Product
15	300	85	84	0.0435	no analysis	Boehmite
54	383	227	120	0.1000	0.0013	Boehmite
52	427	277	120	0.1000	0.0026	Boehmite
51	432	282	120	0.1000	0.0020	Not X-rayed
50	445	297	120	0.1000	0.0027	Boehmite
49	473	327	120	0.1000	0.0037	Boehmite
47	500	350	120	0.1000	0.0035	Not X-rayed
46	503	354	120	0.1000	0.0071	Boehmite-?
59	435	287	144	0.1000	0.0037	Not X-rayed
9	450	302	333	0.0200	0.0177	Pyrophyllite

above the curve. There appears to be no direct ratio in these results, but the data are obviously too few to admit a generalization on the influence of time.

The crucible products were analyzed for silica, and in most cases were X-rayed. In all experiments except 9 and 46, the only product identified by X-ray was boehmite, the monohydrate of alumina. The patterns of this product were sharp and distinctive and compared very well with the pattern of pure synthetic boehmite.

It is known that bayerite at atmospheric pressure loses two molecules of water at 300° C, and the third molecule at 360° C. The present experiments show that under pressure the second stage of dehydration is not reached until the temperature is above 503° at least, for in Exp. 46 a part of the product was boehmite.

The quantities of silica transferred in all experiments except 9 and 46 were apparently too small to produce X-ray lines of the silicate, but pyrophyllite or another silicate may have formed in any or all of the runs. The pattern of the product of Exp. 46 included lines that could not be identified. The three strongest of these lines gave *d* values of 3.24, 2.58, and 3.49 respectively.

The production of pyrophyllite at 450° C in Exp. 9 is in accord with the temperature ranges stipulated by Noll (33) and by Gruner (31). The results agree with those of Laubengayer and Weisz (34), who found that bayerite is unstable above 155° C and that boehmite persists at higher temperatures, unless a seed crystal of diaspore is present when boehmite converts to diaspore above 280° C.

Transfer of Silica to Magnesium Oxide.—The most extensive group of experiments was that in which magnesium oxide was used as the "collector." Magnesium oxide is the crystalline mineral periclase, which is uncommon in nature but may form by the decarbonatization of magnesite during metamorphism (4). At atmospheric pressure this breakdown takes place at 373° C, but, due to the sluggishness of the reaction, may be delayed to a temperature above 500° C (35). Under high CO_2 pressure the stability of the carbonate is doubtless increased; on the other hand the presence of water tends to lower the reaction temperature.

By hydration, periclase is converted to brucite, $Mg(OH)_2$. By the addition of silica, periclase may be converted to any one of a series of hydrous or anhydrous silicates, depending on the temperature and the pressure. Several possibilities are shown by the following equations, which are balanced and arranged to indicate increasing silica requirements:

$$6MgO + 3SiO_2 \rightarrow \underset{\text{Forsterite}}{3Mg_2SiO_4}$$

$$6MgO + 4SiO_2 + 4H_2O \rightarrow \underset{\text{Serpentine}}{Mg_6Si_4O_{11}(OH)_6 \cdot H_2O}$$

$$6MgO + 6SiO_2 \rightarrow \underset{\substack{\text{Enstatite or}\\ \text{Clinoenstatite}}}{3Mg_2Si_2O_6}$$

$$6MgO + 8SiO_2 + 2H_2O \rightarrow \underset{\text{Talc}}{2Mg_3Si_4O_{10}(OH)_2}$$

Jander and Wuhrer (36) have shown that forsterite converts to serpentine in a moderately acid environment at 350° C under pressure but does not convert in a neutral (water) environment at 350° C. Jander and Fett (37), by a series of hydrothermal experiments, found that the reaction

$$\text{Forsterite} \rightleftharpoons \text{Serpentine}$$

between 360° C and 500° C is dependent on temperature and pressure in a rather complex way, although at a given temperature forsterite forms at a lower pressure than serpentine. Synthesis by gaseous transfer was not involved in these experiments.

Present experiments with MgO as the "collector" can be divided on the basis of degree of filling into four sub-groups, which will be considered, first, with regard to quantitative transfer, and, second, with regard to the products formed. All experiments of this group, with the exception of Exp. 118, ran for 72 hours; it is impossible, therefore, to state the effect of variable time. On the basis of Exp. 9, it is believed that increasing the time would, in general, merely raise the curves to higher ordinates. For reference, the experiments of this group can be listed as follows:

Sub-group	Deg. of Filling	Sp. Vol. of Steam	Tables	Figures
I	0.147	6.8 cc/gm	8	4C, 5A
II	0.292	3.43	9	5B
III	0.376	2.66	10	5C
IV	0.424	2.43	—	—

The curves for Sub-group I and for part of Sub-group II-B are reproduced in Fig. 4 C for comparison with other transfer curves.

The curve for Sub-group I (Fig. 5 A) shows accelerated transfer with rise in temperature-pressure. The results of the Sub-group II experiments, given in Table 9, are rather complex, for above 470° C an additional factor, the inversion of cristobalite to quartz,[13] is introduced, and at about the same temperature the transfer from cristobalite reaches a point at which all the 0.0500 gram charge of MgO is converted to forsterite. Accordingly, the relations of this sub-group are shown in Fig. 5 by three curves—B_1, B_2, and B_3.

Curve B_1 representing the transfer of silica from cristobalite to 0.0500 gram of MgO, rises with almost constant slope from 350° C to about 425° C.

[13] In the course of the research it was observed that with higher pressures duplicate results were less frequently obtained; above 470° particularly large discrepancies were noted when conditions were ostensibly the same. For example, Exp. 104 gave only 0.0061 gram transferred, where Exp. 107 gave 0.0332 gram. After repeated attempts to determine the cause of this disturbing effect, it was discovered that high figures resulted when the silica gel inverted only to the metastable cristobalite, and that low values obtained when further inversion to quartz took place. In other words, the inversion to quartz lowers the "solubility" of silica and, consequently, the rate of transfer. Presumably the inversion can occur at any time during the run, and the resulting transfer can be high or low accordingly. Strangely enough, cristobalite can persist in some cases to temperatures as high as 500° C, without inverting to quartz; the reason for its inversion in other cases is not known. (See Notes on Inversion of Silica Gel.)

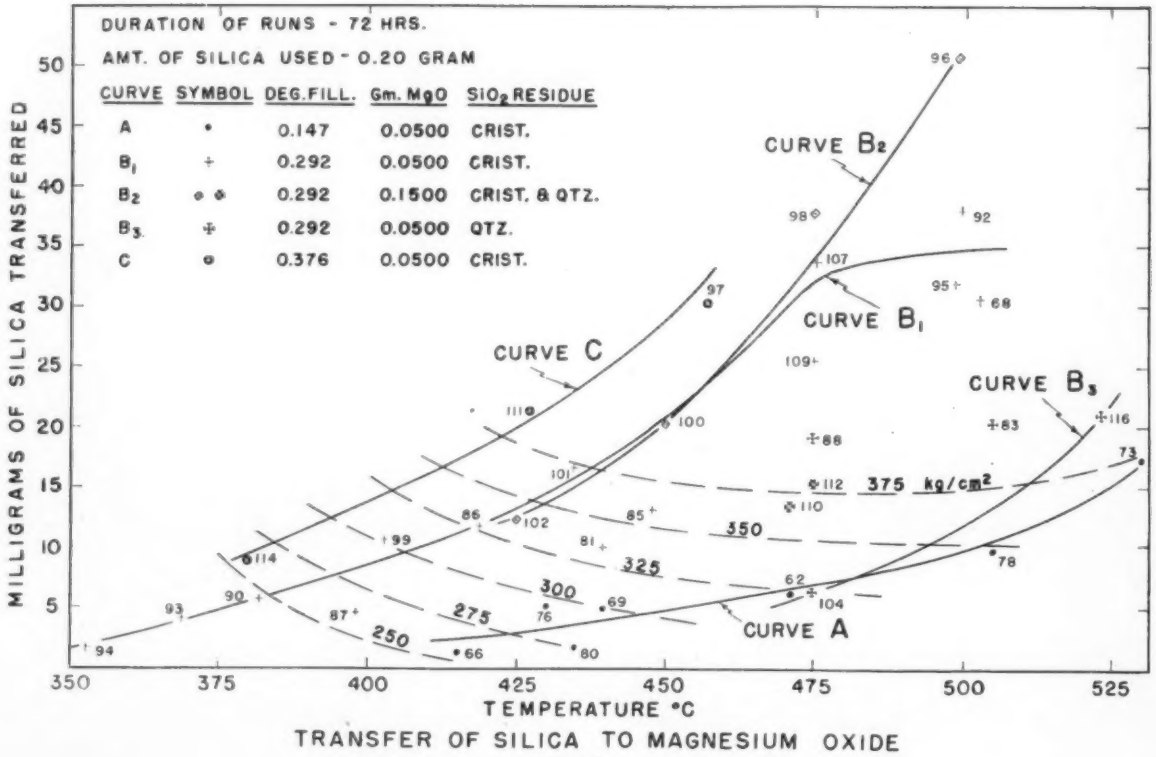

DURATION OF RUNS - 72 HRS.
AMT. OF SILICA USED - 0.20 GRAM
CURVE SYMBOL DEG. FILL. Gm. MgO SiO2 RESIDUE
A • 0.147 0.0500 CRIST.
B1 + 0.292 0.0500 CRIST.
B2 ⊙ ⊙ 0.292 0.1500 CRIST. & QTZ.
B3 ⊹ 0.292 0.0500 QTZ.
C ⊙ 0.376 0.0500 CRIST.
CURVE B2
CURVE B1
CURVE B3
CURVE C
CURVE A
375 kg/cm²
350
325
300
275
250
MILLIGRAMS OF SILICA TRANSFERRED
TEMPERATURE °C
TRANSFER OF SILICA TO MAGNESIUM OXIDE

FIG. 5.

TABLE 8.

GROUP I—TRANSFER OF SILICA TO MAGNESIUM OXIDE WITH DEGREE OF FILLING 0.147.

Amt. of MgO used	0.0500 gram
Amt. of silica gel used	0.2000 gram
Amt. of water used	5.0 cc
Duration of runs	72 hours
Vapor pressure of CO_2 added	2 kg/cm²
Volume of bomb	34 cc

Exp. No.	Temp., °C	Pressure, kg/cm²	Silica Transferred, Grams	Crucible Products	Silica Residue
66	415	267	0.0015	Serpentine and brucite	?
76	430	280	0.0052	Serpentine and brucite	Cristobalite
80	435	286	0.0016	Serpentine and brucite	?
69	440	293	0.0050	Forsterite (trace) and brucite	?
62	472	316	0.0061	Forsterite and brucite	?
78	505	350	0.0099	Forsterite and brucite	?
73	530	375	0.0174	Forsterite and brucite	Cristobalite

TABLE 9.

GROUP II—TRANSFER OF SILICA TO MAGNESIUM OXIDE WITH DEGREE OF FILLING 0.292.

Amt. of silica gel used	0.2000 gram
Amt. of water used	10 cc
Duration of runs	72 hours
Vapor pressure of CO_2 added	2 kg/cm²
Volume of bombs	34 or 34.5 cc

Exp. No.	Temp., °C	Pressure, kg/cm²	Silica Transferred, Grams	Crucible Products	Silica Residue
With 0.0500 gram MgO in crucible:					
94	353	177	0.0018	Brucite and serpentine (trace)	?
93	369	214	0.0041	Brucite and serpentine (trace)	?
90	382	247	0.0058	Brucite and serpentine (little)	?
87	398	288	0.0046	Brucite and serpentine (little)	?
99	403	301	0.0109	Not examined	?
86	419	330	0.0119	Serpentine and brucite	?
101	435	375	0.0167	Forsterite, serpentine and brucite	?
81	440	382	0.0100	Serpentine and brucite	?
85	448	400	0.0132	Forsterite and serpentine (little)	?
88	475	467	0.0191	Forsterite and brucite	Quartz
104	475	467	0.0061	Not examined	Quartz
107	475	467	0.0332	Not examined	Cristobalite
109	475	467	0.0255	Not examined	Cristobalite
95	499	493	0.0320	Forsterite	Cristobalite
92	500	495	0.0380	Forsterite	Cristobalite
68	503	500	0.0308	Forsterite	?
83	505	503	0.0203	Forsterite and brucite	Quartz
With 0.1500 gram MgO in crucible:					
102	425	345	0.0123	Serpentine and brucite	Cristobalite
100	450	407	0.0202	Forsterite and brucite	?
110	471	460	0.0135	Forsterite and brucite	Quartz
98	475	467	0.0378	Forsterite and brucite	Cristobalite
112	475	467	0.0153	Forsterite and brucite	Quartz
96	499	493	0.0506	Forsterite and brucite	Cristobalite
116	523	535	0.0210	Forsterite and brucite	Quartz

Above 425° it ascends more steeply to about 475°, where the amount of silica transferred was sufficient to convert almost all the MgO in the crucible to forsterite. The curve levels off along the 35 milligram ordinate, and passes between points 92 and 95, showing that transfer probably ceased, at least for the duration of the runs, when the MgO had been entirely, or almost entirely, consumed by reaction with silica.

Points 93 and 94 on curve B_1 represent transfer *below* the critical temperature. In both cases liquid water and water vapor were present, and silica could have been transferred only through the vapor. This is especially noteworthy and seems to indicate that silica is probably soluble in vapor, with or without the presence of liquid, providing the vapor is sufficiently dense and the temperature is relatively close to the critical. The curve B_1 passes through the critical region without any apparent disturbance.

By using a larger charge (0.1500 gram) of MgO, points 96, 98, 100, and 102 were obtained. As shown by curves B_2 in Fig. 5, this charge permits a higher rate of transfer in the 500° C region, but does not change appreciably the rate at lower temperatures. Curves B_1 and B_2 are thus coincident below 450° C. It is concluded that the rate of transfer is not much affected by the quantity of "collector," provided there is *enough* "collector" present to fill the requirements of the reaction at a particular temperature. Point 96 probably represents accurately the transfer of silica from cristobalite at 500° C in 72 hours, for the degree of filling 0.292.

Curve B_3 represents approximately the transfer of silica from quartz to MgO, at the conditions of the experiments in which cristobalite inverted to quartz.[14] It shows much lower transfer than curve B_2, indicating the lower solubility of quartz in steam. The slope of curve B_3 between 475° C and 525° C is comparable to the slope of curve B_2 at somewhat lower temperatures, which suggests that the quartz curve, if extended to higher temperatures, might show an overall shape comparable to curves B_1–B_2.

The three experiments comprising Sub-group III show still higher rates of transfer at the higher degree of filling, 0.376. Curve C of Fig. 5, plotted from data shown in Table 10, is similar to curve B_1, but point 97 seems a little low. The values obtained are particularly significant because the degree of filling was so high that liquid water must have flooded the crucible just before the critical temperature was reached. Yet the results are no higher than would be expected with the gaseous phase alone present. It is concluded that the brief incursion of liquid water had no appreciable effect on the results.

Sub-group IV is represented by a single experiment (No. 118). In this experiment 0.2000 gm of silica gel and 14 cc of water were placed in the bottom of a 34 cc bomb, and 0.0500 gm of MgO was placed in the crucible. The temperature was held at 522° C for 120 hours. The degree of filling was 0.424 and the pressure was somewhat more than 650 kg/cm². Liquid water must have flooded the crucible for some time before the critical temperature was reached; therefore, the quantity of silica transferred (0.0589 gm)

[14] Curve B_3 was plotted through point 104, which is the point of minimum transfer at 475° C, and through point 116, which is the only point available at 523° C. This curve is subject to correction by further experimentation.

TABLE 10.

GROUP III—TRANSFER OF SILICA TO MAGNESIUM OXIDE WITH DEGREE OF FILLING 0.376.

Amt. of MgO used	0.0500 gram
Amt. of Silica gel used	0.2000 gram
Amt. of water used	13 cc
Duration of runs	72 hours
Vapor pressure of CO_2 added	2 kg/cm²
Volume of bomb	34.5 cc

Exp. No.	Temp., °C	Pressure, kg/cm²	Silica Transferred, Grams	Crucible Product	Silica Residue
114	380	242	0.0090	Serpentine and brucite	Cristobalite
111	427	390	0.0188	Forsterite, serpentine, and brucite	Cristobalite
97	457	484	0.0302	Forsterite, brucite, and serpentine	Cristobalite

cannot be regarded as a result of gaseous transfer alone. The X-ray photograph of the crucible product shows strong lines of talc and somewhat weaker lines of forsterite.

From the MgO experiments in Sub-groups I, II, and III, it is possible to deduce the relative effects of both temperature and pressure on the rate of transfer. This was not possible with the previous series of experiments, from which only single transfer curves were obtained from any one "collector." Using interpolated points of equal pressure on curves A, B_1-B_2, and C, isobars were drawn from curve to curve as shown in Fig. 5. With increase in pressure, a gradual flattening of the isobars appears within the temperature range covered, up to the 375 kg/cm² isobar. In other words, for any isobar below 375 kg/cm² the transfer *decreases* with rise in temperature, but this depressing effect of temperature lessens gradually with pressure increase and at 375 kg/cm² the transfer is approximately the same for curves A, B, and C. The few available points on curves B and C indicate that for isobars above 375 kg/cm² the transfer *increases* with rise in temperature.

The crucible products of these experiments are listed in the accompanying tables. Brucite formed at all temperatures when excess magnesia was present. In Sub-group I, serpentine formed below 440° C and forsterite formed at and above 440° C. The transition pressure was about 290 kg/cm². In all experiments of this sub-group the silica residue was cristobalite.

In Sub-group III experiments, serpentine formed at temperatures as high as 457° C and forsterite developed with serpentine at temperatures as low as 427° C. There is, then, an overlap wherein both forsterite and serpentine may form. The transition is influenced somewhat by pressure, for the stability range of serpentine is clearly extended upward by higher pressures.

NOTES ON THE INVERSION OF SILICA GEL.

The temperature and pressure at which silica gel first inverts to a crystalline form was not determined in the experiments, but it seems that the first inversion is always to cristobalite. The examination of silica residues from runs not exceeding 80 hours duration showed that cristobalite alone forms

within the temperature range from 350° to 530° C when the pressure does not exceed 375 kg/cm², and within the range from 350° to 450° C when the pressure does not exceed 400 kg/cm². On the other hand cristobalite may persist to a temperature of 500° C or more when the pressure is as high as 500 kg/cm²; or it may invert to quartz when the temperature exceeds 450° C and the pressure is greater than about 400 kg/cm². The inversion of cristobalite to quartz, within the temperature range of the experiments, is more dependent on pressure than on temperature, but other unknown factors seem to influence the change.

Optical examination of the cristobalite discloses a dense, white, chert-looking material with conchoidal fracture. The inversion to quartz produces a multitude of tiny grains, some of which are euhedral, others subhedral, and still others apparently anhedral. The inversion also produces a volume decrease, which is shown by a network or anastomosis of intergranular spaces.

The residue from Exp. 10, which ran 14 days, was a loosely bound aggregate of euhedral, prismatic quartz crystals, which individually measured 0.05 mm long and almost as wide. The *r* and *m* crystal faces predominated and *s* faces were subordinate.

DISCUSSION.

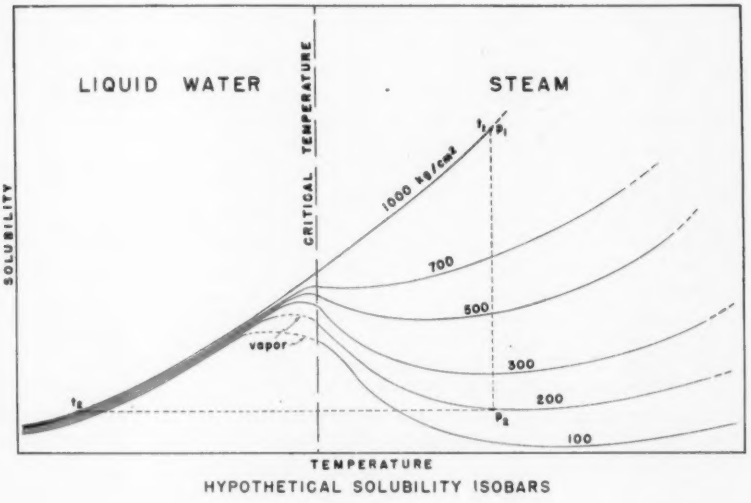
The experiments on solubility must be regarded as reconnaissance runs and the single results from the barium chloride and sodium carbonate experiments need verification. However, the experiments with silica provide further evidence of the solubility of silica in superheated steam.

In experiments of this sort, the question naturally arises: In what combination do the silicon and oxygen atoms or ions exist in solution in steam? It seems that silica is transferred and deposited in the molecular proportions of SiO_2, but the actual arrangement of the atoms in solution is not known. Some physical chemists, including Glasstone (11, p. 382), conceive of a series of tetrahedra, each composed of one silicon atom to four oxygen atoms, so arranged that any silicon-2 oxygen combination would be unsatisfied and would have to unite in some manner with the atoms of the solvent.

It is noteworthy that the silica shows different rates of transfer to different "collectors." If various "collectors" in a single bomb were exposed simultaneously to steam-borne silica, it is probable that the distribution of transferred silica among the various "collectors" after a given time would be in accordance with some sort of "reaction potential series." The establishment of such a series is a field for future research.

Referring now to Figs. 3 C and 5, it will be noticed that there is an approximate parallelism between the solubility isobars for quartz, derived from the date of van Nieuwenburg and van Zon, and the "transfer isobars" for silica obtained from present experiments. The transfer of a substance certainly bears a relation to the solubility of that substance and if the general trend of the isobars in either figure is extrapolated to include, say, the 700 kg/cm² isobar, it is evident that that isobar would show a positive slope in

the supercritical range. The general hypothetical picture seems to be that shown in Fig. 6. The solubility isobars, which in the liquid range are fairly contiguous (since pressure has relatively little effect on the solubility of a non-volatile substance in a liquid), diverge at about the critical temperature. The isobar of lowest pressure, upon entering the supercritical temperature range, falls off to a minimum and does not resume a positive slope below a fairly high temperature. Other isobars of relatively higher pressures diverge into a family of curves showing relatively higher minima at relatively lower temperatures. The isobars for pressures above about 1000 kg/cm² probably show no such negative slopes after passing the critical point, but continue upwards from the liquid range into the gas range. In other words, at the pressure at which this congruency is established the gas state becomes identical with the liquid state as regards solvent ability. This is the relation recognized long ago by Hannay.



HYPOTHETICAL SOLUBILITY ISOBARS

FIG. 6.

The solubility of a non-volatile substance in a gas is more dependent on pressure than on temperature, at least up to the point at which the liquid-gas congruency is established.

The above considerations lead to the interesting corollary that, whereas the physical precipitation of material from a liquid solution is brought about principally by decrease in temperature, the precipitation from a gas can be effected by decrease in pressure alone. Referring to Fig. 6, assume that a non-volatile substance is held in solution in steam at supercritical temperature t_1 under 1,000 kg/cm² pressure. Let the pressure fall to 200 kg/cm² without

any appreciable fall in temperature, *i. e.*, isothermally. This would be possible if the walls of the container were maintained at constant temperature. A decrease in pressure represented by the dotted line p_1–p_2 and a corresponding decrease in solubility would result. The same decrease in solubility could be effected, of course, by a fall in temperature from t_1 to t_2.

CONCLUSIONS.

1. At supercritical temperatures and pressures, and to a lesser extent in the high subcritical range, steam can take into solution and transport considerable quantities of certain non-volatile substances including silica, potash, potassium carbonate, and barium chloride. Under the conditions of the experiments, however, sodium carbonate and aluminum hydroxide do not show detectable solubility in steam.

2. At constant pressures below 500 kg/cm² and within the temperature range from the critical to at least 450° C, the solubility of quartz or of silica gel in steam apparently *decreases* with rise in temperature. For the pressure range above about 500 kg/cm² or for the temperature range above 450° C the isobaric solubility probably *increases* with rise in temperature.

3. Whereas the physical precipitation of material from a liquid solution is brought about mostly by decrease in temperature, the precipitation from a gas can be effected by decrease in pressure alone.

4. Kaliophilite forms in neutral environment at 450° C and about 300 kg/cm² pressure when silica is scarce and potash and alumina are plentiful. Pyrophyllite forms under the same conditions when potash is not present, and muscovite develops at supercritical temperatures as high as 575° C when alumina is plentiful and potash and silica are made available slowly, as by transfer through steam.

5. Bayerite does not exist at supercritical temperatures but the monohydrate, boehmite, can exist, perhaps as a metastable form, to temperatures at least as high as 500° C and to pressures as high as 350 kg/cm².

6. Wollastonite forms at 450° C by reaction of steam-borne silica with calcium carbonate (Iceland spar), and probably forms in the same way over a considerable range of temperature. High concentrations of carbon dioxide inhibit this reaction.

7. In the presence of high-temperature steam, magnesium oxide converts to brucite at some temperature below 353° C, and the brucite is apparently stable to temperatures at least as high as 530° C. If silica is introduced through steam, brucite changes to serpentine or to forsterite, depending on the temperature and pressure. Contrary to the conclusions of Jander and Fett (37), forsterite seems to form at higher pressures and temperatures than serpentine, but there are overlaps, and the temperature range of serpentine formation is increased upward by rise in pressure. Talc forms with forsterite at still higher pressures and temperatures.

8. Silica gel, on heating under hydrothermal conditions, crystallizes first as cristobalite, which, for 72 hours at least, can persist to temperatures as high as 450° C. At temperatures above 450° C the cristobalite inverts

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eventually to quartz if the pressure is sufficiently high; but in some experiments cristobalite persisted for 72 hours at temperatures as high as 500° C and at pressures as high as 495 kg/cm².

9. The rate of transfer of silica to magnesium oxide through steam is roughly proportional to pressure, and for pressures above 375 kg/cm², within the temperature range of the experiments, increases with rise in temperature; but for pressures below 375 kg/cm², within this temperature range, the rate of transfer decreases with temperature. The rates of transfer to sodium carbonate, calcium oxide, and aluminum hydroxide increase with temperature-pressure for a constant degree of filling, but the effect of temperature alone or of pressure alone cannot be determined from the curves for these substances.

10. The rate of transfer of silica from quartz is lower than the rate of transfer from silica gel. It is concluded that the rate of transfer of a non-volatile substance depends upon the relative solubility of that substance in the gas and on the "reaction potential" of that substance with regard to the "collector."

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PSEUDO-EUTECTIC AND PSEUDO-EX-SOLUTION INTERGROWTHS OF NICKEL ARSENIDES DUE TO HEAT EFFECTS.[1]

J. E. HAWLEY AND D. F. HEWITT.

ABSTRACT.

Pseudo-eutectic and pseudo-ex-solution intergrowths of Ni_3As_2 in NiAs and Ni(As,Sb) solid solutions, corresponding respectively to the natural minerals, maucherite and niccolite, are described and compared with a natural intergrowth of these minerals. The intergrowths were produced by heat treatment of solid solutions of NiAs with up to 30 atomic per cent NiSb. They are due to partial dissociation of the NiAs or Ni(As,Sb) at temperatures ranging from 500° C to over 850° C according to a peritectic reaction involving the formation of Ni_3As_2 and arsenic vapour. On further addition of antimony to the nickel arsenide lattice the structure is stabilized and dissociation does not occur.

The suggestion is made that similar natural intergrowths of both maucherite in niccolite and of some pentlandite in pyrrhotite may be primarily due to the heat effect of later invading ore solutions or a decrease in containing pressures while the ores are still at elevated temperatures.

INTRODUCTION.

THE purpose of this paper is to present new data on some interesting and significant textures developed in natural and artificial metallic minerals of the system NiAs, Ni_3As_2 and NiSb which were obtained unexpectedly in an attempt to establish the solubility of NiAs and NiSb in artificial preparations, substances which occur in nature as niccolite and breithauptite as individual species individually or together in cobalt and nickel ores.

Experimental Procedure.—Materials used for the experiments were chemically pure powdered metallic nickel, arsenic and antimony which were mixed thoroughly in various atomic proportions ranging from pure NiAs to NiSb. Charges weighing one gram were placed in silica glass tubes, evacuated and sealed. Heating was then carried out in a Lindberg furnace to the temperatures required for reaction or fusion to occur and the charges were allowed to cool slowly (5–10 hours) in the furnace. Annealing of the products was later carried out at various temperatures and over varying periods of time.

Fusion products were split, one part was polished and examined under a metallographic microscope, the other was available for X-ray study and density measurements on the Berman balance.

EXPERIMENTAL RESULTS.

NiAs-NiSb Solid Solution Series.—As will be shown in a separate paper by Hewitt a complete solid solution series extending from NiAs to NiSb was

[1] Presented before the Geological Society of America, Ottawa meeting, December, 1947.

produced. Comparison of the artificial end members with natural minerals, niccolite from Hesse and breithauptite from Cobalt, both by X-rays and in polished sections shows them to be identical.

Separation of Ni_3As_2 from NiAs and Arsenic-rich Solid Solutions.—In synthesizing NiAs it was found that on heating the constituents in evacuated and sealed tubes to high temperatures a two-phase aggregate consisting of NiAs and Ni_3As_2 formed. As noted by Vigouroux in 1908, according to Hansen (1)[2] NiAs on heating to about 850° undergoes partial dissociation with the loss of arsenic and the formation of the trinickelo-diarsenide Ni_3As_2 according to the peritectic reaction [3]:

$$3NiAs \rightarrow Ni_3As_2 + \uparrow As$$

The product Ni_3As_2 so formed is the equivalent of the mineral, maucherite.

Melts consisting of 90, 80 and 70 atomic per cent NiAs, with 10, 20 and 30 atomic per cent NiSb, likewise yielded two-phase aggregates, *but with*

TABLE I.

FUSIONS AND HEAT TREATMENT.

Composition	Maximum Temp. °C.	Phases	Heat Treatment	Products
NiAs (Nat.)	950	2 Phases	—	NiAs, Ni_3As_2
NiAs (Art.)	1210	2 Phases	500°–20 hours	NiAs, Ni_3As_2
NiAs (Art.)	750	1 Phase	500°–10 hours	NiAs, Ni_3As_2, x
NiAs (Art.)	500	1 Phase	750°– 8 hours	NiAs, Ni_3As_2, x
NiAs (Art.)	500	1 Phase	500°–20 hours	NiAs, Ni_3As_2, x
90NiAs.10NiSb	1150	2 Phases	500°–20 hours	Ni(As, Sb), Ni_3As_2
90NiAs.10NiSb	500	1 Phase	750°– 8 hours	Ni(As, Sb), Ni_3As_2, x
80NiAs.20NiSb	1130	2 Phases	500°–20 hours	Ni(As, Sb), Ni_3As_2
80NiAs.20NiSb	500	1 Phase	750°– 8 hours	Ni(As, Sb), Ni_3As_2, x
70NiAs.30NiSb	1130	2 Phases	500°–20 hours	Ni(As, Sb), Ni_3As_2
60NiAs.40NiSb	1130	1 Phase	500°–20 hours	Ni(As, Sb)
50NiAs.50NiSb	1080	1 Phase	500°–20 hours	Ni(As, Sb)
40NiAs.60NiSb	1210	1 Phase	500°–20 hours	Ni(As, Sb)
30NiAs.70NiSb	1210	1 Phase	500°–20 hours	Ni(As, Sb)
20NiAs.80NiSb	1210	1 Phase	500°–20 hours	Ni(As, Sb)
10NiAs.90NiSb	1210	1 Phase	500°–20 hours	Ni(As, Sb)
NiSb (Art.)	1080	1 Phase	500°–20 hours	NiSb

x—Detected only with X-rays.

greater concentrations of NiSb only one phase, a solid solution, was produced. Temperatures attained were varied from 1210° C to 500° C as noted in Table I. The experiments indicated that at about 400° C arsenic vaporizes in the evacuated tubes and reacts with the nickel to form nickel arsenide.

Since in the initial experiments rapid heating to 1100–1200° C had been used, two other series of tests were made at lower temperatures in an endeavor first to prepare a Ni(As,Sb) solid solution, and then by heat treatment to cause this to break down into Ni_3As_2 and arsenic.

[2] Numbers in parentheses refer to Bibliography at end of paper.
[3] So named by Hansen.

The first of these tests was made with pure Ni and As in the proportions of NiAs in sealed tubes, heated to 750° C for 8 hours. Granular pellets of artificial niccolite were formed. Subsequently, after briquetting, these were annealed in evacuated and sealed tubes for 10 hours at 500° C. X-ray examination of the products showed only a small amount of Ni_3As_2.

A second series of powders, consisting of 100, 90 and 80 atomic per cent NiAs with 0, 10 and 20 atomic per cent NiSb, were heated in evacuated and sealed pyrex tubes to 500°–550° C for a few hours. The products appeared homogeneous and X-ray photographs showed no discernible artificial maucherite lines. Reheating, however, at 500° C for 20 hours caused some breakdown as shown by X-ray analysis, faint lines of Ni_3As_2 appearing with those of NiAs.

It is apparent that NiAs begins to dissociate when heated in vacuo for appreciable periods of time at temperatures ranging from 500° C to 1200° C. In no case did the reaction go to completion, and no attempt was made to establish the equilibrium relations between NiAs and Ni_3As_2 and arsenic vapor.

From both the initial tests and subsequent heat treatment given other mixtures of NiAs and NiSb (Table I) it is clear that addition of NiSb in amounts between 30 and 40 atomic per cent stabilizes the lattice of the solid solutions resulting, so that dissociation to Ni_3As_2 and arsenic does not occur either at temperatures of 1100–1210° C, or on annealing at 500° for 20 hours.

In those charges containing NiSb in amounts of 30 atomic per cent or less, from which Ni_3As_2 was formed, it is not known whether the antimony remained with the "niccolite" phase as a solid solution or entered the "maucherite" phase as well. Analyses of natural maucherite (Dana's System of Mineralogy, 1944) do not indicate any antimony present. In the Ni-Sb system, however, as reviewed by Hansen (1936) a phase (γ) is formed at high temperatures with 58.5 to 60 per cent weight Sb which approaches Ni_3Sb_2 in composition. It is hence probable Ni_3As_2 will tolerate some Sb in its composition. The very gradual change in lattice dimensions of NiAs, with increased amounts of Sb in products in which Ni_3As_2 formed, further supports the view that Sb during the peritectic reaction does not become concentrated to any extent in the "niccolite" phase, though this may bear further investigation.

TEXTURES RESULTING FROM DISSOCIATION OF NIAS AND NI(AS,SB).

Examination of the fusion products of charges containing 100 to 70 atomic per cent NiAs, in polished sections, showed the pinkish NiAs phase and greyish-violet Ni_3As_2 which gave identical etch reactions with the minerals niccolite and maucherite respectively. Though the two differ considerably in anisotropism and are readily distinguished in polarized light with crossed nicols, staining for a few seconds with $FeCl_3$ reagent served as an excellent aid in studying the intergrowths in ordinary reflected light.

In the arsenic rich preparations, as in pure NiAs, three types of intergrowths were observed, one consisting of rounded to curving club-shaped particles of Ni_3As_2 (C, Fig. 1) distributed in a pseudo-eutectic manner throughout grains of the NiAs phase, which by replacement have partly or wholly isolated

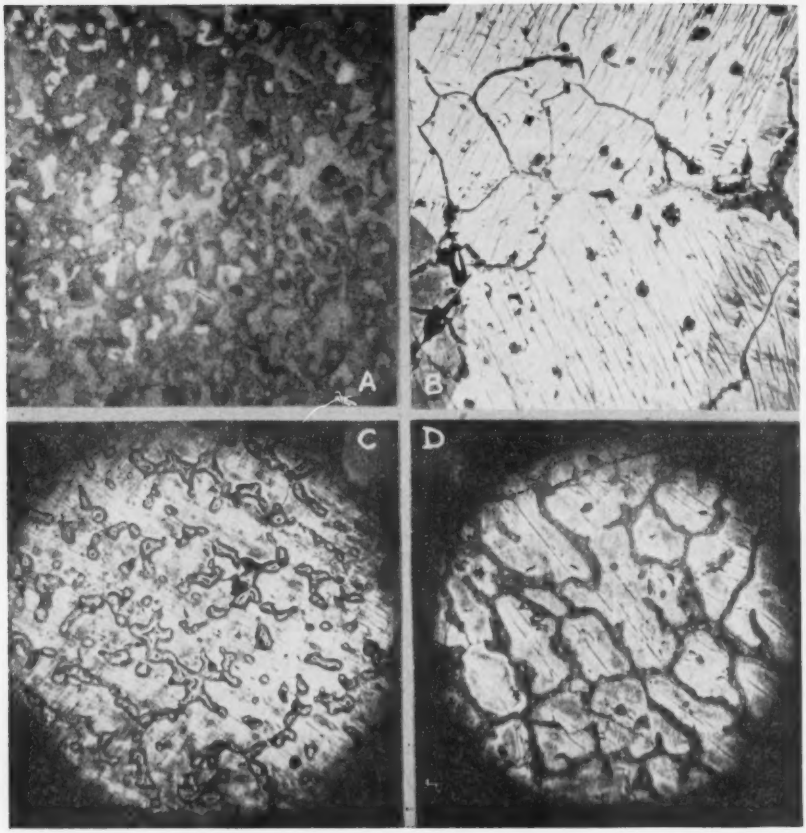

FIG. 1.

A: Pseudo-eutectic intergrowth of niccolite (gray) and maucherite (stained black with $FeCl_3$) with chalcopyrite (white) replacing niccolite and rarely maucherite—Sudbury ore. × 130.

B: Fine "ex-solution-type" blades of artificial maucherite (black) in solid solution of 70NiAs·30NiSb. × 85.

C: Pseudo-eutectic intergrowths of Ni_5AS_2 in solid solution 80NiAs·20NiSb. × 70.

D: Cell, pseudo-cell and blade textures of Ni_5As_2 in solid solution 90NiAs·10NiSb. × 70.

fragments of NiAs, and which in part follow grain boundaries and give rise to a rather distinct cell or net texture as shown in D, Fig. 1. This second texture is clearly similar in origin to the first and really a variety of it. Its similarity to cell or net textures formed by ex-solution processes is apparent. The third texture is a bladed type, in which fine plates of Ni_3As_2 follow one orientation within Ni(As,Sb) grains (B, Fig. 1).

Pseudo-eutectic and Cell or Net Intergrowths.—Since these two pass insensibly from one to the other they are best treated together, the only distinction drawn being that the former term refers to rounded oval or irregular club-shaped segregations of Ni_3As_2 within single grains of NiAs, and the latter to similar segregations confined in part to Ni(As,Sb) grain boundaries.

These formed in pure NiAs, and in the 90 and 80 per cent NiAs charges, and to only a very minor extent in the 70NiAs·30NiSb mixture. A short etch with $FeCl_3$ brings out a banded structure within the segregated phase of Ni_3As_2, the outer rim of which consists of slightly darkened and roughened columnar crystals, not unlike the columnar structure recorded for natural maucherite, surrounding a still smooth white interior (C, Fig. 1). Within the latter in some cases is a central area which stains quickly black with $FeCl_3$ (resembling a cavity in C, Fig. 1) and tarnishes brown with HCl. X-ray analysis of material from the three zones indicates only Ni_3As_2 but the small size of the bands has so far prevented more accurate determination. The differences in behavior may be entirely due to differences in orientation of Ni_3As_2 or to slight differences in the ratios of Ni to As and Sb.

A more advanced dissociation of Ni(As,Sb) than shown in C, Fig. 1, gives rise to the well defined cell or pseudo-cell texture in which the Ni_3As_2 phase follows grain boundaries or advances and give rise to several cells within one grain of Ni(As,Sb). This was best developed in the product obtained from a charge of 80 NiAs·20 NiSb (D, Fig. 1).

Bladed Intergrowths.—Fine blades of Ni_3As_2 intergrown in (Ni,Sb) were developed in three products consisting of 70, 80 and 90 atomic per cent NiAs, but not in the pure NiAs. This texture is shown in B, C and D, Fig. 1, and is almost the sole development of Ni_3As_2 in B which is composed of 70 atomic per cent NiAs, suggesting that up to a point, increase in antimony favors this texture as compared with others.

In other sections, not illustrated, it appears that early or partial formation of the Ni_3As_2 phase takes place with the development of exceedingly fine, closely spaced blades within Ni(As,Sb) grains, leaving clear borders, but further dissociation enlarges these and they may then extend directly to the borders and merge with marginal Ni_3As_2. The unique orientation of the Ni_3As_2 plates suggests it has formed along basal planes, the only unique direction in the NiAs lattice.

The resemblance of this texture to ex-solution Widmanstatten textures formed by the break-down of solid solutions is apparent, and like the cell or net texture may be appropriately described as a *pseudo-ex-solution* texture formed by the dissociation of the arsenic rich Ni(As,Sb) solid solutions with loss of arsenic.

CRITERIA FOR THE RECOGNITION OF AGE AND GENETIC RELATIONS OF ORE MINERALS.

From the foregoing it is readily apparent that since textures strongly resembling both pseudo-eutectic textures due to replacement and ex-solution textures of the cell and blade type may be readily produced in metallic minerals which partially dissociate on heating (or melt incongruently to form another solid and gas), some revision in our concepts of the genetic significance of these types of textures is called for and further experimental work on similar metallics is warranted.

Comparison with Natural Pseudo-eutectic Intergrowths of Niccolite and Maucherite.—Examination of some niccolite rich specimens from the Sudbury district (Garson Mine) has shown the presence of a pseudo-eutectic intergrowth of maucherite in niccolite as illustrated in A, Fig. 1. Attention is called to the resemblance of the irregular club-shaped particles of maucherite, stained black, to similar aggregates in the artificial intergrowth of C, Fig. 1. In addition to these two minerals, chalcopyrite (white) is present replacing niccolite and in other sections forms an identical type of intergrowth with niccolite alone, as noted by Lausen (2) in ores from the Worthington mine. Rarely, as indicated by Lausen, does the chalcopyrite replace the maucherite, though one instance is noted in the upper right corner of C, Fig. 1.

All would probably agree that the maucherite-niccolite intergrowth is replacement in origin. Normally it would be attributed to a post-niccolite invading solution. The possibility that it is simply due to either heat effects of such solutions or to a decrease in confining pressures, which were exceeded by arsenic vapor pressure while the deposit was still at high temperatures, is obviously an alternative explanation. In the instance cited, the later introduction of chalcopyrite may have supplied the heat necessary for the dissociation of niccolite and the formation of maucherite.

Comparison with Natural Ex-solution Intergrowths.—The marked resemblance of the cell or pseudo-cell and the bladed intergrowths produced artificially to natural intergrowths is so marked that distinction as to genesis could likely be made only on a basis of the physico-chemical relations of the two phases involved. Where the intergrowth is due to true ex-solution the two phases must be capable of forming a solid solution, where due to a peritectic reaction on heating, such a relation should be demonstrable.

To the writers' knowledge there is no natural example of a bladed "ex-solution-type" of texture which may be attributed alone to partial dissociation of a previously formed metallic ore mineral. One natural example which should receive mention in this connection, however, is that of bladed, vein-like and flame-like intergrowths of pentlandite in pyrrhotite. Previous investigations of the artificial counterparts of these minerals (Hawley, Colgrove, Zurbigg (3)) suggested nickeliferous pyrrhotites with a wide range in nickel content could be formed. This was corroborated by G. S. Colgrove (4) in later work, and has recently been confirmed by D. Lundquist (5) by X-ray analysis of artificial preparations. Experiments recently completed by V. A. Haw in our laboratories have clearly shown that loss of sulphur from such solid solutions

on heating in sealed tubes results in the formation of blades, vein and flame-like segregations of "pentlandite" which differ in no marked respect from natural intergrowths. Since the migration of nickel atoms is involved as well as the loss of sulphur the segregation of "pentlandite" in artificial pyrrhotite is a case of true ex-solution, but the cause of the unmixing may be attributed directly to the heat effects such as might arise in natural ores by either later mineral introductions (*e.g.*, chalcopyrite) or the lowering of containing pressures. Experimental investigation of other metallic minerals may indicate other groups which fall in this category.

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KINGSTON, ONT.,
Mar. 1, 1948.

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MINERAL RELATIONSHIPS IN THE ORES OF PACHUCA AND REAL DEL MONTE, HIDALGO, MEXICO.[1]—A REPLY.

EDWARD WISSER.

A MINING district as viewed through the ocular of a microscope is apt to differ surprisingly from the appearance it presents to one who has trudged over its surface and climbed through its stopes for ten years. To such a one the laboratory microscopist suggests a man sizing up this complex world by peeking through the keyhole of his front door. The Pachuca-Real del Monte mineralized district covers nearly 50 square kilometers. The aggregate area of the 34 polished surfaces on the basis of which Dr. Bastin draws generalizations regarding that district is perhaps 50 square inches or some 300 square centimeters.

An understanding of the geography of a district must underlie conceptions of its geology. In Table I (p. 55) Dr. Bastin lists the mines from which his specimens were taken, in two columns headed respectively "Pachuca District" and "Real del Monte District." Four mines and veins listed under Pachuca belong in Real del Monte (Dolores-Tapona vein; La Rica-Vizcaina vein; Santa Margarita-Salvadora vein; San José de Gracia). One mine, Camelia, with its Maravillas vein, is listed under Pachuca and Real del Monte. It lies in Pachuca.

The Amistad and Barron mines, listed under Pachuca, belong in an area not mentioned, the Santa Gertrudis area, southeast of Pachuca and southwest of Real del Monte.

In an effort to unscramble Dr. Bastin's geography and as a general aid in this discussion, the present writer offers the accompanying plan. Dr. Bastin's Table I is rearranged below. All mines mentioned by him are located on the plan or their position described in the Table, except the Jesús María, the position of which I do not recall.

Pachuca Area

Santa Ana
Camelia-Maravillas vein
Calderona (west end of El Cristo vein)
Santa Rita
Cuauhtemotzín
Rosario (includes San Pedro)
Jacál (part of Analcos-Rosario linked vein system)
Porvenir

Real del Monte Area

Morán
Dificultad (Santa Inés vein near coordinate 11,000N)

[1] Edson S. Bastin: ECON. GEOL., vol 43, No. 1, pp. 53–65, January–February, 1948.

San José de Gracia
San Pedro y San Pablo (Gran Compaña fault-vein at coordinate 22,000E)
Sacramento (Santa Brígida vein between Gran Compaña and Viscaina fault-veins)
Carretera (Santa Inés vein just north of Vizcaina)
Aguichote (just east of Santa Inés and north of Vizcaina)
La Rica-Dios te Guíe vein. (La Rica mine contains La Rica vein, the segment of the Dios te Guíe north of the Vizcaina, and a segment of the latter vein)
Colón
Santa Margarita-Salvadora vein
Dolores-Tapona vein

Santa Gertrudis Area

Amistad
Barron

With the geography straightened out it becomes possible to deal with the geology and mineralogy in relation to the district as a whole. I have written extensively on the district [2-9] and shall not attempt to summarize once more my general ideas concerning it, but rather to comment on Dr. Bastin's paper *seriatim*.

"Within these volcanic rocks, particularly the relatively extensive older andesite, are east-west zones of extensive and profound hydrothermal alteration and it is within these altered zones that the mineral veins occur" (p. 54).

Fig. 1 shows the principal fractures and dikes of the district, the main ore bodies and the areas of thorough hydrothermal alteration.

It is difficult to find a perfectly fresh specimen of andesite anywhere in the Sierra de Pachuca. Everywhere the feldspar phenocrysts are more or less sericitized, calcitized, etc., or the ferromagnesian phenocrysts chloritized or otherwise altered. The areas of alteration shown on the plan are those within which the groundmass of the rock is altered as well as the phenocrysts. Specifically, these areas show "bleaching" and chloritization. By "bleaching" is meant a change from the original dark green to black color of the andesites to very light tints. The "bleaching" may be caused by sericitization, calcitization or kaolinization of phenocrysts and groundmass or to combinations of the

[2] Edward Wisser, Formation of the North-South fractures of the Real del Monte area etc.: Am. Inst. Min. Met. Eng. Trans., vol. 126, pp. 442–486, 1937.

[3] Edward Wisser, Use of the microscope to discover faults cut by diamond drill holes: Econ. Geol., vol. 32, No. 5, pp. 570–578, August 1937.

[4] Edward Wisser, Discussion of paper by H. E. McKinstry, Structural control of ore deposition is fissure veins: Am. Inst. Min. Met. Eng. Trans., vol. 144, pp. 91–93, 1941.

[5] Edward Wisser, contribution to symposium, Some observations in ore search: Ibid., pp. 143–145.

[6] Edward Wisser, The environment of ore bodies: Am. Inst. Min. Met. Eng. Tech. Pap. 1026, pp. 99–102, 108, 1939.

[7] Edward Wisser, Discussion of paper by David Gallagher, Albite and gold: Econ. Geol., vol. 36, No. 6, pp. 658–663, September–October 1941.

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[9] Edward Wisser, Discussion of paper by C. L. Thornburg, Some applications of structural geology to mining in the Pachuca-Real del Monte area, etc.: Econ. Geol., vol. 41, No. 1, pp. 77–86, (January–February 1946.)

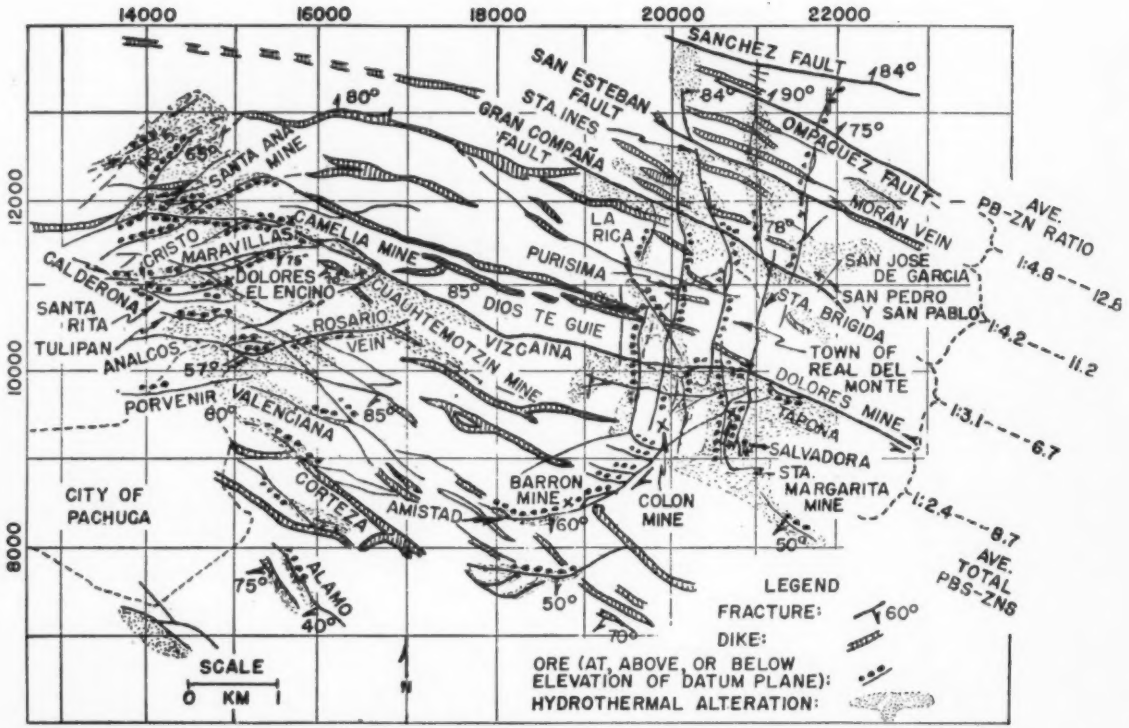

FIG. 1. Pachuca-Real del Monte District, Mexico. Fractures and dikes projected to datum plane at 2360 m elevation.

three. "Bleaching" and chloritization, while to some extent mutually exclusive, have about the same significance with respect to fracturing and mineralization, and hence were mapped as a unit.

It is evident from the plan that the fracture system controls the distribution of hydrothermal alteration; but some areas of alteration spread out with apparent disregard of any particular major fracture. The largest such areas (1) in Santa Ana, (2) near the Analcos vein and (3) in southeastern Real del Monte, coincide with areas of intense, although principally minor, fracturing.

Altering solutions ascending a master fissure which cuts across ground otherwise essentially unfractured did not spread very widely away from their channel. They did their work on the immediate walls of the fissure and on fragments of wall rock within the fissure. Examples are the Maravillas, Rosario and Corteza veins in the Pachuca area.

In contrast, altering solutions rising through an area intensely and minutely fractured, with or without master fissures, tended to spread through the fractured area, guided by the network of minor fractures.

Viewing hydrothermal alteration in the district as a whole, the trend, if any, of areas of hydrothermal alteration is north-south, both in Pachuca and in Real del Monte. Perhaps the most significant feature connected with hydrothermal alteration in the district is the lack of important alteration associated with the Purísima and Santa Inés ore bodies. This matter is discussed below.

"The largest ore shoots were found in the East-West veins and reached 1,000 meters along the strike" (p. 55). The largest single ore bodies in East-West veins were those in the Vizcaina in the northern Pachuca area and in the Santa Gertrudis vein (the Barron mine exploited the east end of this ore body). Each of these slightly exceeded 1,000 meters in length. But the North-South Purísima ore body was also over 1,000 meters long, and the North-South Santa Inés and Santa Brígida ore bodies nearly as long. Further, the North-South ore bodies have on the average twice the vertical extent of the East-West ore bodies.

"Of the 34 polished specimens examined under the reflecting microscope only one showed evidence of fracturing during hypogene mineralization, and other specimens from the same mine showed no such evidence. Cyclic repetitions of the mineral sequences do not occur" (p. 55).

There follow a few field and microscope notes made by the writer, from the same series of mines, as nearly as possible, from which Bastin's specimens came.

PACHUCA AREA.

Santa Ana.—The typical Santa Ana vein is a quartz-cemented breccia of silicified rock fragments. The cementing quartz is fine, even-granular. The relative abundance of massive pyrite, a vein mineral introduced mainly with the first surge of mineralization in the district suggests that the Santa Ana vein fractures were in existence at the start of mineralization. Repeated

brecciation of the veins and the presence of many types of quartz of various relative ages confirm this notion.

The earliest quartz introduced at Santa Ana is fine-grained, white, glassy or grayish, or coarse-grained glassy; the latest type, directly associated with ore sulphides in stringers that cut across all earlier vein matter, is fine-grained to aphanitic, usually dark.

Camelia.—The veins in Camelia mine north of the Vizcaina not only show ore localization explainable by horizontal intramineral movement along the vein fractures and along transverse fractures [10] but one of them exhibits horizontal striae on vein quartz, indicating that these movements continued after deposition of at least some of the quartz.

Maravillas.—Quartz occurs in a number of generations, each accompanied by reopening of the vein. At the start of mineralization some massive pyrite was introduced (as is the case in all older veins of the district). Sphalerite, the next sulphide in age, predominates over galena. For tectonic reasons for considering the Maravillas an older vein fracture, see reference of footnote 2, page 454 and Fig. 5.

Analcos-Rosario.—Here galena is more plentiful than blende and there are fewer generations of quartz. The vein attains great widths and in places shows crustified banding. For these and other reasons (reference of footnote 2, pages 483–484) the Analcos-Rosario vein fissure is thought to be relatively young, and to have been opening late in the period of metallization, just in time to catch the rich silver-lead surge. The walls of the fissure were pulling apart as the vein matter entered; this accounts for the crustified banding (see footnote 11, below). As at Santa Ana and commonly throughout the district, the latest quartz is intimately associated with ore sulphides, is fine-grained to aphanitic and dark in hue.

Porvenir.—A miniature of the Analcos-Rosario vein system.

REAL DEL MONTE AREA.

Santa Inés Vein, Dificultad.—Commonly a sheeted zone in andesite, with closely-spaced quartz-sulphide stringers along the sheeting planes; the zone contains one or more wide bands of quartz-cemented rock breccia. This structure is masked where mineralization is intense, in the heart of the ore; the vein is solid quartz from wall to wall because the rock fragments in the breccia bands and the rock slabs between the sheeting stringers have been entirely replaced by vein matter. It is only toward the fringes of such strong mineralization, toward the north or south end of the ore body, that the key to vein structure may be obtained; here the successive introduction of quartz and sulphides through repeated openings of earlier vein matter is clearly apparent. Naturally a few random specimens studied under the microscope might completely miss any such diagnostic localities.

The Santa Inés vein in Dificultad carries but little massive pyrite, in contrast to the same vein north of the Gran Compañía fault-vein (Fig. 1); the lead-zinc ratio of the Santa Inés and other North-South veins between the

[10] Reference of footnote 8, Figs. 5–8, page 233.

Gran Compaña and Vizcaina fault-veins is lower than for the same veins north of the Gran Compaña (see ratios on plan) but higher than for North-South veins south of the Vizcaina. Since the early surge of mineralization was characterized by abundant iron and zinc, the later by lead and silver, it follows that fractures in existence from the start of mineralization should show heavy pyrite and blende, and that those coming into existence at a later period should show scantier pyrite and blende, and more abundant later vein minerals such as galena and argentite. Hence, the mineralogy described suggests growth of the North-South Real del Monte vein fractures, in general from north to south. Tectonic reasons for thinking the same are set forth in the reference of footnote 2 (pp. 471–473 and elsewhere).

San Pedro y San Pablo (Gran Compaña fault-vein).—The Gran Compaña is one of the older northwest fractures of Real del Monte (reference of footnote 2, page 470). The mineralized stretches along this fault show repeated brecciation and many quartz types; silicification of the walls is commonly intense, as might be expected with an older fault in existence before the start of vein formation. Sphalerite greatly predominates over galena.

Sacramento (Santa Brigida vein between Gran Compaña and Vizcaina fault-veins).—Data are sparse because the ore bodies have been mined out for many years. On the 400 m level (2,360 m elevation, datum plane for the plan projection) the vein is a breccia of quartz fragments cemented by later quartz.

Carretera (Santa Inés vein just north of Vizcaina).—The description is the same as that for the same vein in Dificultad.

Aguichote.—On the 400 m level this vein consists of quartz, pyrite, base sulphides and rhodonite cementing angular fragments of silicified andesite. Stringers of quartz, pyrite and base sulphides cut indiscriminately across all earlier vein matter.

Dios te Guíe Vein, La Rica Mine.—In places, this vein is a mineralized rubble-filled fissure, with intense replacement of fragments and walls. The breccia is mainly cemented by quartz and sulphides, but in places drusy cavities lined with very large quartz prisms mark interstices between the breccia fragments. Some of these *abras* are tabular openings in the vein, 20 cm wide and 1 m long.

The Dios te Guíe, Purísima and other North-South veins of central Real del Monte show less intramineral fracturing than do most veins in the district. From tectonic considerations it is thought that in this area North-South vein fractures came into existence only at the time of the rich silver-lead surge of metallization, and that they were opening *pari passu* with the introduction of vein matter during that surge, which was of brief duration. This tectonic conception agrees with the fact that the vein matter associated with the great silver ore bodies in these veins is uniform in composition and shows relatively little intramineral shattering. There was simply one great opening of these fissures during which the rich vein matter came in more or less as a body.

A further confirmation of this notion derives from the fact that hydrothermal alteration of the walls next these ore bodies is slight and in places

lacking; there were no fractures here at the time of intense alteration (hydrothermal alteration preceded vein formation throughout the district).

Vizcaina Vein in La Rica Mine and Elsewhere.—The Vizcaina carries a great variety of quartz types; the main ore body is localized by zigzag structure indicating horizontal intramineral movements along the Vizcaina fault (reference of footnote 2, Fig. 14, p. 473).

Colón Mines (Colón veins Nos. 2, 3).—These veins lying south of the Vizcaina, are combinations of sheeted zones and bands of quartz-cemented rock breccia. Stringers of dark sulphides in many places cut all older structures within the vein. Replacement of the rock fragments and of the rock between the sheeting is intense. Galena is still more abundant in relation to sphalerite (Fig. 1) than in central Real del Monte north of the Vizcaina, suggesting a relatively late age for the Colón veins.

Santa Margarita Mine-Salvadora Vein.—In places this vein carries an *abra* along its hanging wall containing abundant galena. Toward the bottom of the ore, the vein consists of a breccia of silicified andesite fragments cemented by white quartz and sulphides. The silicified rock fragments have been shattered repeatedly, with recementation.

SANTA GERTRUDIS AREA.

The Barron and Amistad mines were not accessible to the writer.

These examples suffice to show that intramineral vein reopenings are the rule in the district. Unfortunately, Dr. Bastin dealt with veins that were torn open on a megascopic rather than a microscopic scale; a common width for a late sulphide stringer cutting across all other vein matter is just about the diameter of a polished specimen. Many of Dr. Bastin's specimens doubtless came from such late stringers and he extrapolates data from the specimen across the whole width of the vein.

Microbrecciation is indeed rather rare in the Pachuca-Real del Monte veins. Where it exists it shows the following features: brecciation of quartz with recementation by finer-grained quartz; the healed gash is usually visible under cross nicols only ("ghost veinlets"); marked strain effects in interference tints; tiny conjugate "shear planes."

Such effects are far less common in the veins than in adjacent more or less mineralized wall rock, for a reason advanced below.

Among the veins that do exhibit microfracturing are the Santa Ana veins and those of Camelia; the Maravillas, Encino, Tulipán, Valenciana, all in Pachuca. In Real del Monte, corresponding veins are the Purísima, Santa Inés, Dios te Guíe, Vizcaina, Santa Brígida and Colón No. 3.

Many specimens from these same veins show no microfracturing, the reason being, as I have said, that the intramineral shattering was on too large a scale to show up in general under the microscope.

In contrast, wall rocks close to major faults and fault-veins show very marked microfracturing, much of which, in the case of fault-veins, was intramineral. Thus in my paper (reference of footnote 3) I show that out of

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several hundred thin sections examined, from specimens collected with impartiality throughout the district, without regard to nearness to or distance from faults and veins, 109 showed some degree of microfracturing. Nearly three-quarters of these came from points within 20 m of a fault. Large blocks of ground away from faults, and proportionally represented in the group of specimens, showed no microfracturing whatever.

The dominant type of microfracturing exhibited consists of two sets of fracture planes, intersecting at angles varying from 45° or less to 80°. The thin sections, oriented at random, rarely show the true angle between the conjugate planes. In general the angle seen in the section is less than the true angle.

In places the two sets of planes are equally developed; in others one set is strong, the other weak; sometimes only one set appears, but its representatives maintain a uniform trend throughout the thin section.

These fracture sets appear chiefly in the plagioclase phenocrysts, but with severe fracturing the fractures pass through phenocrysts and groundmass alike. In places, mainly near fault-veins, the fractures carry quartz or carbonate. Elsewhere the feldspar (andesine-labradorite originally) has altered to albite along the fracture planes. Albitization of the feldspars is an important feature of hydrothermal alteration in the district, a feature closely linked areally to ore bodies.

Quartz phenocrysts rarely show fracturing along simple planes. They are as a rule irregularly fractured, often shattered to form mosaic areas. Where the plagioclase phenocrysts show fractures but not the quartz phenocrysts, the latter often show strong interference strain effects.

Microfracturing in the immediate walls of veins has been noted in the case of the Santa Ana veins, where bunches and small stringers of quartz show microbrecciation with recementation by finer-grained quartz. One specimen shows fracturing of feldspar phenocrysts but little of vein quartz, a fact the significance of which will be shown below.

The Vizcaina vein in Camelia is properly a lode, with several major strands separated by mineralized country rock. A specimen from the latter shows a fracture pattern suggesting shear planes within the feldspars and a groundmass that appears to have yielded by flow.

Even the vein strands of the Vizcaina lode contain many horses of country rock; a specimen from one of these horses shows conjugate shear planes. One set is well developed, the other poorly developed and exhibiting horse-tailing reminiscent of Butte. Some planes of each set carry carbonate.

A specimen taken from a small vein near the Vizcaina shows phenocrysts in a fractured andesite horse, the fractures carrying albite, calcite and quartz, whereas adjacent vein quartz is unfractured. A specimen taken from the north strand of the Vizcaina lode shows microbrecciation of vein quartz but none of adjacent calcite.

Similar microfracturing of wall rocks characterizes many other fault-veins of the district.

As pointed out in the paper cited (reference of footnote 3), this microfracturing, so markedly limited to the vicinity of faults, is a fault-drag feature (Fig. 2). Where renewal of movement is initiated along a pre-existing, older fault plane, the stress sets up a strong shearing strain in a tabular body of rock enclosing the fault plane, and actual rupture on this plane ensues only at the culmination of the shearing strain in its walls. (Where stresses that lead toward faulting concentrate on a zone of weakness with no pre-existing fault defining that zone, the zone is deformed by "plastic flow" exactly as in the first case; only at the culmination of the "plastic" deformation the resulting fault in this case comes into being for the first time, with rupture and displacement occurring on it as soon as it forms).

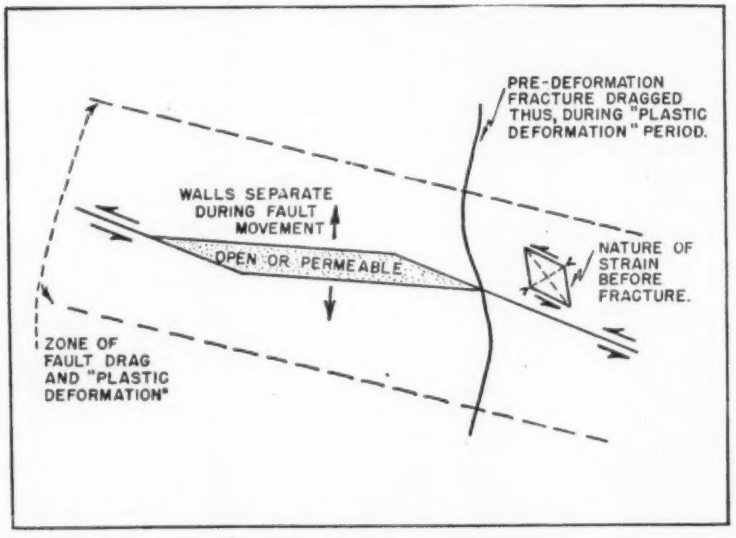
PRE-DEFORMATION FRACTURE DRAGGED THUS, DURING "PLASTIC DEFORMATION" PERIOD.
WALLS SEPARATE DURING FAULT MOVEMENT
OPEN OR PERMEABLE
NATURE OF STRAIN BEFORE FRACTURE.
ZONE OF FAULT DRAG AND "PLASTIC DEFORMATION"

FIG. 2.

In either case, the pre-displacement "plastic" deformation deforms a tabular body of rock. With porphyritic andesite the brittle phenocrysts yield by fracture, the glassy groundmass by "flow." That the building up of such stress along the older dip-slip faults of Real del Monte at the time of the later strike-slip fault movements, an accumulating stress which culminated in rupture along the older faults, coincided in time with the period of mineralization is brought out in references 2, 6, 8 and others.

The tabular body of rock deformed by stresses that lead to faulting records the strain it has undergone, where the rock is andesite, in an especially sensitive manner. The glassy, amorphous groundmass is prone to "flow"; but where it has been softened prior to major fault movements and to metal-

lization by hydrothermal alteration, it will "flow" much more readily. Brittle feldspar phenocrysts set in such a "plastic" matrix fracture all the better for the contrast in physical properties with their surroundings. The easily "flowing" groundmass makes them yield, and they can yield only by fracture.

Strong, homogeneous vein quartz in wide veins would fracture much less readily under the same shearing stress. Strain may accumulate in the soft wall rock along a fault-vein before a body of massive quartz along that vein yields at all. In such cases, when the quartz body does yield, it tears apart, or is "sheared" along major planes of differential fault movement, as gougy, tight seams in many veins attest. Commonly the quartz on either side of such an intravein fault plane is little deformed.

While strain is accumulating in the wall rock next a fault surface upon which movement is about to take place, or within a body of rock within which a fault is about to be born, there is little opportunity for vein minerals to deposit. That is why the tiny fracture planes in wall rock feldspars close to Pachuca-Real del Monte fault-veins carry albite, an early mineral, together with quartz and carbonate, but seldom or never ore sulphides, even the early pyrite. Once differential fault movements are initiated they may, and usually do, come in successive jerks. There is little or no accumulation of strain in the fault walls between each jerk; the succession of jerks involves one and the same period of faulting.

Once the fault movements have started, opportunity for metallization is at hand. Quartz-sulphide bodies typically deposit along faults in places of local tension—where the walls tend to pull apart rather than glide tightly, one past the other. The "zigzag control" shown in Fig. 2 is merely one of a number of possible examples, but it may illustrate the principle involved.

Mineralizing solutions ascending in the area will select the open or permeable segment of the vein shown, a segment made more open or permeable as differential movements proceed.

Berg [11] believes that crustified banding in veins occurs only where the vein fissure is opening during entry of vein matter, and then only when opening was faster than filling. Where opening was slower than filling, the opening tore new cracks in older vein matter, resulting in the late stringers cutting older material that have been mentioned. The Analcos, Vizcaina in Real del Monte, and the Morán veins (the latter mentioned by Dr. Bastin) show crustified banding; with them, opening presumably proceeded faster than filling; most other veins of the district fail to show crustified banding but do show repeated tearing apart of older vein matter, the rents being healed by younger material. Here following Berg's ideas, filling was faster than fissure opening.

Where a fissure was about to form by stretching of the country rock, *e.g.*, by bending due to vertical upward shove, the resulting tension in porphyritic andesite would be reflected in microfracturing of the phenocrysts and flow of the groundmass; the vein that filled the tension fissure when the latter did form would resemble that just described; crustified banding would be present

[11] Georg Berg, Vein filling during the opening of fissures: ECON. GEOL., vol 27, No. 1, pp. 87–94, 1932.

where the walls were being pulled apart faster than solutions were fed in; the vein would be ripped and torn, with the tears healed by later vein matter, where solutions came in faster than the fissure was being opened.

In the light of the present writer's field experience, and especially that part of it gained in the Pachuca-Real del Monte district, Berg's notions have the ring of truth. Most epithermal veins, at least, look like one or the other of Berg's two classes. The fact that replacement, as Bastin says, was of great importance in the formation of the veins of that district does not affect the mechanics of vein formation outlined above, because the intensity of alteration by vein-forming solutions was a direct function of the permeability of the vein fractures. The solutions never entered static zones of sheeting; they never peacefully permeated undisturbed rock to deposit their load by replacement free from tectonic domination.

If these ideas are correct, intramineral movements accompany the formation of crustified banded veins, veins which would show no evidence of such movements in Dr. Bastin's specimens. Intramineral movements involving the other type of vein, that showing repeated pulling apart of earlier vein matter and healing of the rents by later material, took place, in the Pachuca-Real del Monte district at least, on a megascopic, not a microscopic scale; they are visible in a stope, but not under a microscope.

". . . argentite is found occasionally in these ores as a supergene replacement of other sulphides but its commonest modes of occurrence are as a component of the compact ores and as crystals in small vugs" (page 56).

It is doubtful whether any supergene argentite exists in the district. The fact that argentite is the latest sulphide seen in a specimen is no proof that it is supergene. Argentite kept on depositing in the district after even most of the late galena had ceased to be deposited. Veins which from tectonic considerations are thought to be relatively late have as almost their sole sulphides galena and argentite, and the galena does not greatly predominate over the argentite.

Most of the veins described by Dr. Bastin, those mined in recent years, are "blind" veins. They do not outcrop; otherwise they would have been found and their ore mined many years ago. (Among the blind veins, specimens from which are described by Dr. Bastin, are: Santa Ana veins, Aguichote, Dios te Guie, Colón, Tapona of Dolores mine, and Salvadora of Santa Margarita.)

The top of ore on the Santa Ana vein fractures failed to reach the present surface by over 200 meters; that on the Colón and Salvadora veins of southern Real del Monte, by nearly 400 meters. In the highest mine levels the vein fracture in each case is very weak, and diligent search on the surface, where premineral rock formations are exposed, failed to find any fracture corresponding to the upward extension of the vein fracture, in each of these cases.

The tops of these ore bodies were only spottily oxidized and leached; this might be expected since waters descending from the surface lacked a consistent channel through which to reach the vein fractures. For the most part argentite remained, before it was removed by stoping, unaltered at the very

tops of these ore bodies, and it differed in no respect from argentite found at the bottoms of the ore bodies.

"In some such porous ores, silver as wires and teeth is abundant as a supergene mineral" (page 57).

Native silver occurs in the district in two forms: wire silver (including "teeth") and plate silver, the latter as thin dendritic films.

Plate or dendritic silver was best exhibited associated with the Alamo vein (Fig. 1). This vein was for the most part a buried outcrop; it lay on the side of a former deep canyon now filled with recent clays, tuffs, etc., so that this wall of the canyon was a dip slope with respect to the vein. The Alamo ore was completely oxidized, and the top of the ore lay at an elevation lower than that of the bottom of ore on other veins in the area, north of the Alamo. There are reasons for believing the entire Alamo ore body was moved down the dip of the vein fracture by supergene agencies. The ore ceased downward when oxidation ceased, and the barren primary vein matter showed practically no sulphides except sparse pyrite.

Dendritic, platy native silver was abundant in this oxidized ore, and especially in the fractured dacite of the footwall, adjacent to the main ore body. The thin plates of silver coated fracture faces in the dacite. This dendritic silver was without doubt transported and deposited by supergene solutions.

In contrast, wire silver is confined to sulphide ore bodies, which, if oxidized, are oxidized in their uppermost portions only and contain wire silver in places scattered from the top to the bottom of the ore. The silver wires are sometimes seen resting on aggregates of argentite crystals within a vug. Silver wires are never seen out in the walls, away from an ore body. Thus wire silver was abundant in the Tapona ore body of Dolores mine, on the 300 meter level. This level is 300 meters below the surface and 150 meters below the top of the ore body. There is little or no oxidation on the 300 m level.

Carpenter and Fisher [12] in their metallographic study of native silver examined a number of specimens. Although plate silver occurs as either supergene or hypogene, the single specimen of wire silver contained in the group was concluded by them to be hypogene.

Douglas,[13] during his stay of many years at Pachuca, produced wire silver on the sides of artificial argentite buttons by subjecting them to moderate heat (125°–135° C) in the open air. By straining the buttons (filing them with a coarse file) the rate of growth of the wires was increased. Since the wires grew in the space between the buttons and the crucibles in which the latter had solidified, he concluded that they grew after cooling, solidification and shrinkage of the argentite buttons. No solutions, hypogene or supergene, affected the formation of these wires. While Douglas's wires might be ascribed to an oxidation effect, in nature silver wires perched on unaltered

[12] Sir H. C. H. Carpenter and Dr. M. S. Fisher, A metallographic investigation of native silver: London Inst. Min. Met. Trans., vol. 41, pp. 382–402, 1931–1932.

[13] C. B. E. Douglas, Native wire silver notes on its formation and possible significance: London Inst. Min. Met. Trans., vol. 42, pp. 398–402, 1932–1933.

argentite might with logic be ascribed to a giving out of sulphur in solutions which had deposited argentite while the sulphur lasted.

"According to W. F. Foshag . . . *adularia* occurs in microscopic crystals in some of the altered (sic) vein material" (p. 60). The present writer showed this mineral, visible in thin sections only, to Foshag in 1935. While other optical properties would seem to indicate adularia rather than albite, by a slight margin, the mineral in question is optically positive, like albite, not negative like adularia. The mineral, I feel certain, is albite; its presence as an early mineral within the veins would not be unexpected, considering the extensive albitization of plagioclase feldspars in wall rocks near veins.

Concerning most of Dr. Bastin's mineralogy and paragenesis I have no particular question. The chief point of the present discussion has been emphasized before but apparently needs reemphasis, namely, microscopic study of ore specimens is a valuable adjunct to field work. But when carried on without field knowledge of the district involved, it is apt to give so distorted a picture that its publication confuses and retards understanding of the district rather than advances it.

UNIVERSITY OF CALIFORNIA,
BERKELEY, CAL.,
April 1, 1948.

SYNTHESIS OF LEAD SULPHANTIMONITES.[1]

S. C. ROBINSON.

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ABSTRACT.

Lead sulphantimonites were synthesized by dry fusion in vacuum and from various aqueous solutions in a closed system at temperatures up to 425° C and at pressures up to 2,000 bars, and the products were correlated with natural minerals by X-ray powder and Weissenberg photographs. Only two lead sulphantimonites were synthesized by dry fusion in vacuum: boulangerite and "mineral X," a new mineral from the Red Bird mine, Nevada, which has not as yet been named. From aqueous solutions artificial equivalents of fuloppite, plagionite, semseyite, zinkenite and "mineral X" were synthesized, together with two other lead sulphantimonites for which natural counterparts are unknown. Products of hydrosynthesis were sealed in vacuum and subjected to temperatures below their melting points (about 380°) for a period of two weeks. Outward crystal form of these products remains unchanged, but in every case partial to complete alteration to boulangerite, "mineral X" or galena, with deposition of a brown sublimate of stibnite had occurred.

The minerals reproduced by hydrosynthesis are typical of the epithermal environment; minerals of mesothermal association were not obtained in this way. Sulpho-salts form most readily from alkaline and variably sulphurous solutions; acid solutions result in deposition of lead and antimony sulphides with, rarely, traces of lead sulphantimonites. Neutral chloride salts facilitate formation of these sulpho-salts; carbonates and bicarbonates repress such formation.

[1] Part of a thesis supervised by Professors J. E. Hawley and L. G. Berry and accepted for the degree of Ph.D., Queen's University, 1947, and presented before the Geological Society of America, Ottawa meeting, December 1947.

INTRODUCTION.

In the study of mineral genesis, mineral syntheses are useful in amplifying and extending the natural evidence on which current theories are based. While it is impossible to duplicate in the laboratory all postulated natural conditions, it is possible to evaluate by experiment many of the inferences drawn from natural phenomena and, again empirically, to add to the knowledge of the chemistry of various chemical systems involved. Such syntheses are also useful in providing artificial material, the examination of which, serves to extend and to verify incomplete descriptions of natural material.

Previous synthetic work has shown that most simple ore minerals can be reproduced artificially under widely differing conditions whereas conditions of formation of such complex minerals as the sulpho-salts are much more critical. Certain lead sulphantimonites have been synthesized by fusion of PbS and Sb_2S_3 but there is no record of attempted hydrosynthesis of these minerals. Differences in solubility of lead and antimony in aqueous solutions are generally much greater than those between silver and antimony. It is to be expected, therefore, that conditions of formation of the lead sulphantimonites should be even more critical than those of the silver sulphantimonites studied by Béland (1).[2] In nature certain lead sulphantimonites appear to be restricted to the mesothermal zone of deposition and others to the epithermal zone, while more than one of these minerals have been reported from deposits classed as xenothermal. Varying synthetic conditions of formation of the different lead sulphantimonites may thus be correlated with the varying conditions of the different zones in natural deposits.

In the field of descriptive mineralogy, the lead sulphantimonites are notable for the large number of mineral names proposed for supposedly differing mineral entities. Of twenty such names only five remain whose identity has been adequately established, other names remain open to question; still others have been previously discredited. Minerals in the Pb-Sb-S system are generally poorly developed and intimately intergrown; comparison with their synthetic equivalents, therefore, should afford the opportunity both of adding to descriptions of natural material and of investigating the validity of questionable species. This phase of the investigation, together with data regarding methods of identification of the products, has been described previously (13).

The five established mineral lead sulphantimonites are:

Boulangerite	$10PbS \cdot 4Sb_2S_3$	(2)
Semseyite	$9PbS \cdot 4Sb_2S_3$	(11)
Plagionite	$5PbS \cdot 4Sb_2S_3$	(11)
Zinkenite	$4PbS \cdot 4Sb_2S_3$	(11)
Fuloppite	$3PbS \cdot 4Sb_2S_3$	(10)

Omitted from this list are the two end members: galena, PbS, and stibnite, Sb_2S_3, together with two other fully established species which, however, have been found to contain additional elements; meneghinite, $Cu_2S \cdot 26PbS \cdot 7Sb_2S_3$ (4) and jamesonite, $4PbS \cdot FeS \cdot 3Sb_2S_3$ (3).

[2] Numbers in parentheses refer to "Bibliography" at end of paper.

In the course of this investigation, three other lead sulphantimonites and one sodium sulphantimonite were synthesized. Of these one lead sulphantimonite was found to be identical with a natural mineral, as yet not named from the Red Bird mine, Pershing Co., Nevada. The natural material was made available through the courtesy of Dr. Schaller of the United States Geological Survey.

These additional products are:

Mineral X	$7PbS \cdot 6Sb_2S_3$ approx.
Phase I	$6PbS \cdot Sb_2S_3$ approx.
Phase II	$5PbS \cdot 4Sb_2S_3$ approx.
Phase III	$Na_2S \cdot 2Sb_2S_3$ approx.

Figure 1 shows the compositions of both the natural and artificial lead sulphantimonites plotted on a ternary diagram.

Due to difficulties in identification of these minerals, occurrences reported in field descriptions must be accepted with reserve. A survey of such descriptions, however, does show that fuloppite, zinkenite, plagionite and semseyite

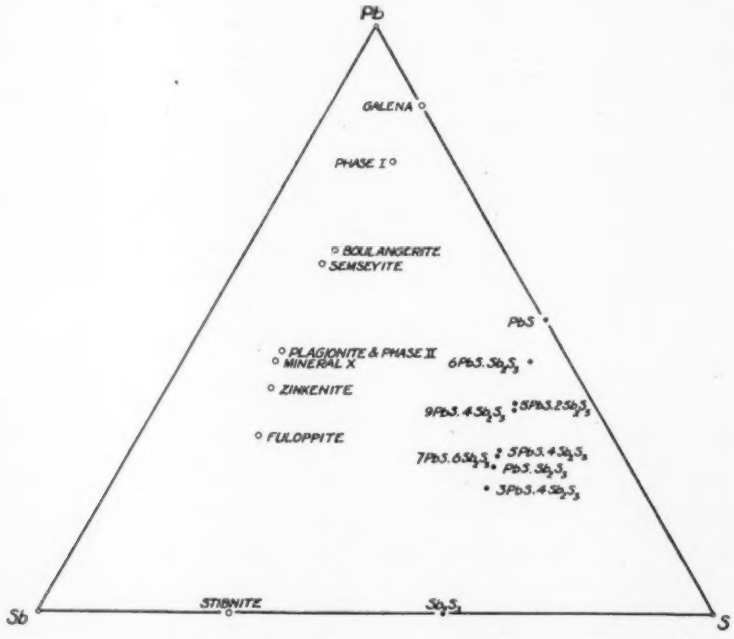


FIG. 1. Ternary diagram showing minerals and artificial compounds of the Pb-Sb-S system:
(a) by weight per cent (open circles),
(b) by mol per cent (filled circles).

are commonly found in deposits of epithermal character, while boulangerite, jamesonite and meneghinite are more typical of mesothermal association. In such xenothermal deposits as those of Oruro and Potosi, Bolivia, all of these minerals have been reported. Finally there appears to be little doubt from field evidence that lead sulphantimonites are of primary hydrothermal origin.

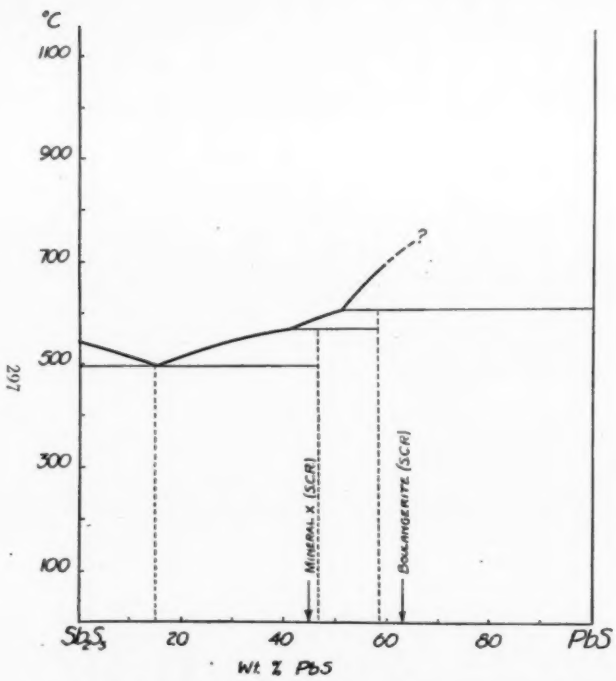
Of previous synthetic investigations of the Pb-Sb-S system the work of Sommerlad (16), Jaeger and Van Klooster (7), Iitsuka (6) and Schenk (14) should be noted. X-ray determination of products was lacking in all these investigations; determination of products obtained is, therefore, questionable. Sommerlad (16) reported many compounds prepared both by direct fusion of PbS and Sb_2S_3 and by the action of $PbCl_2$ vapor on solid Sb_2S_3. Products of the latter method were shown by Ducatte and Rondel (quoted by Jaeger and Van Klooster, 1912, p. 253) to be other than lead sulphantimonites; determination of products reported by direct fusion is entirely inadequate. Jaeger and Van Klooster (7) reported synthesis of "jamesonite" ($2PbS \cdot Sb_2S_3$) and plagionite ($5PbS \cdot 4Sb_2S_3$) by direct fusion of PbS and Sb_2S_3 in an open system; their work was corroborated by adequate thermal data. Iitsuka (6), apparently using the same methods as Jaeger and Van Klooster, reported zinkenite, "warrenite" ($3PbS \cdot 2Sb_2S_3$), "jamesonite" ($2PbS \cdot Sb_2S_3$) and boulangerite. Finally Schenk (14) and his co-workers reported plagionite, "plumosite" and boulangerite as products of heating a mixture of PbS and Sb_2S_3 at 400° C and desulphurizing by means of a stream of hydrogen gas. No adequate determination of these products is described.

In the investigations to be described below, the writer employed direct fusion of PbS and Sb_2S_3 in an evacuated, closed system, deposition from various aqueous solutions, also in a closed system, in which the maximum temperatures and pressures involved were of the order of 425° C and 2,000 bars respectively, and, finally, the heating of the products of hydrosynthesis in evacuated tubes at temperatures well below the minimum for the liquidus-solidus curves of the system.

SYNTHESIS BY DIRECT FUSION OF PbS AND Sb_2S_3.

Equilibrium diagrams redrawn from those published by Jaeger and Van Klooster and Iitsuka are reproduced in Figs. 2 and 3. In Fig. 2 the compounds synthesized by the writer, by the method of direct fusion, are also indicated. Recent determinations of the melting points of PbS and Sb_2S_3 are 1120° C and 550° C respectively (Chem. Eng. Handbook 1941); Iitsuka's equivalent values of 1050° C and 516° C indicate that the temperatures which he records throughout the system are correspondingly low. Temperatures recorded by Jaeger and Van Klooster are in good agreement with recent determinations.

The two diagrams are largely in accord over the range from 0 to 60 per cent PbS by weight. For fusions containing more than 60 per cent PbS, Jaeger and Van Klooster observed that reactions were so sluggish that changes in slope of the cooling curves are so gradual as to be beyond interpretation. It is in this range that Iitsuka reports a second eutectic. Table I contains pertinent extracts from the thermal data on which the two equilibrium diagrams are based.



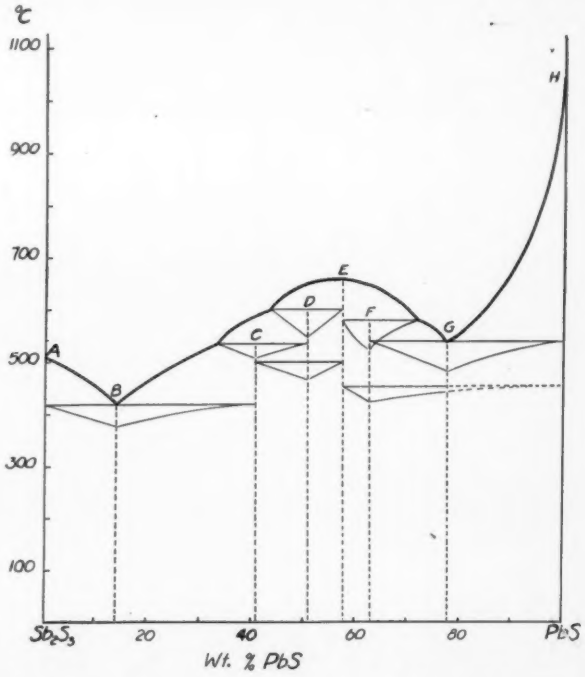


FIG. 2 (left). Equilibrium diagram for the PbS-Sb_2S_3 system. Redrawn from thermal data of Jaeger and Van Klooster (1912) and showing products obtained by the present writer.

FIG. 3 (right). Equilibrium diagram for the PbS-Sb_2S_3 system, after Iitsuka (1919).

Both investigators obtained a compound "jamesonite" having a composition $2PbS \cdot Sb_2S_3$. It is also possible that Iitsuka's "warrenite" is equivalent to the plagionite of Jaeger and Van Klooster. The latter authors do record some slight indications of a peritectic reaction in the range of Iitsuka's zinkenite. Reference has been made to the virtual impossibility of accurate determination of the various lead sulphantimonites except by use of X-ray powder photographs; since this technique was not available to either of these earlier investigators, their determination of products must be treated with reserve.

TABLE I.

Wt. % PbS	Mineral	Temperature °C			
		Primary Crystallization	Transition		Eutectic
100 (J&V.K.)	Galena PbS	1120	—	—	—
100 (I)	Galena PbS	1051	—	—	—
78 (I)	Eutectic	557	—	—	—
63 (I)	Boulangerite $5PbS \cdot 2Sb_2S_3$	590	596.8	468	—
58 (J&V.K.)	Jamesonite $2PbS \cdot Sb_2S_3$	609	—	—	—
58 (I)	Jamesonite $2PbS \cdot Sb_2S_3$	672	—	—	—
51 (I)	Warrenite $3PbS \cdot 2Sb_2S_3$	660	610	513	—
46.7 (J&V.K.)	Plagionite $5PbS \cdot 4Sb_2S_3$	590	565	522	391
41.0 (I)	Zinkenite $PbS \cdot Sb_2S_3$	594.6	546.1	—	—
20 (J&V.K.)	Eutectic	495	—	—	—
14 (I)	Eutectic	428	—	—	—
0 (J&V.K.)	Stibnite Sb_2S_3	546	—	—	—
0 (I)	Stibnite Sb_2S_3	516.3	—	—	—

Materials and Methods Employed.—Materials used by the writer in synthesis by fusion were:

Crystalline Sb_2S_3, analysis of which showed 99.7 per cent Sb_2S_3, 0.1 per cent free sulphur, 0.2 per cent remainder.
Lead metal 99.99 per cent pure.
Flowers of sulphur, Baker's C.P.

Charges were made up from 5 per cent to 95 per cent PbS by weight in steps of 5 per cent PbS content and, additionally, others conforming exactly to the compositions of all minerals and eutectics reported in the system. These charges were based on a total weight of one gram. To duplicates of certain of these one-gram charges, excess sulphur was added in amounts up to 0.5 gm. Components were weighed and charged separately, sulphur first, followed by Sb_2S_3 and lead, in order to reduce volatilization when sealing off the tubes.

Fusion was carried out in "Vitreosil" tubes which may be quenched at 1200° C without fracture. Tubes were sealed under a vacuum of the order of 1 mm of mercury by an oxy-hydrogen flame. It was found impracticable to seal a thermocouple into these tubes; no attempt, therefore, was made to record cooling curves. The charged tubes were heated in an electric furnace

with a built-in thermocouple. All fusions were heated to about 1200° C and held at that temperature for about 20 minutes in order to ensure complete melting of any PbS which might have formed and thus to secure liquid miscibility. Duplicate charges were variably cooled; some were allowed to cool slowly to room temperature, others were cooled rapidly to 750° C and then cooled to 400° C over periods up to 48 hours, still others were quenched at 1200° C, reheated to 750° C and cooled slowly to 400° C.

On cooling to room temperature, the fusions were broken out of the tubes and examined under a binocular microscope. They were then split, one-half being mounted in bakelite and polished, the other half being used for composite X-ray powder photographs and for reference.

X-ray powder photographs were made both of composite material from the fusion as a whole and from individual products scratched from the etched polished sections. By comparison of these photographs, the possibility of overlooking other phases, which might be present in significant amounts but which might not be recognized in etched section, was avoided.

Products Obtained.—Over fifty different fusions were made and in these only four phases were recognized, stibnite, "mineral X" ($7PbS \cdot 6Sb_2S_3$), boulangerite and galena. Examination of etched sections, corroborated by X-ray powder photographs, showed that in none of these fusions was the product homogeneous. Five charges were fused in attempts to synthesize homogeneous "mineral X" but none of these was successful; either the eutectic or boulangerite was present in addition and in two cases, three phases were present together. The precise composition of boulangerite being known, one of three identical charges corresponding to its composition was quenched at 1200° C, another cooled slowly to room temperature over a period of 48 hours, and the third was quenched at 1200° C, reheated to 750° C and cooled to 400° C in 48 hours. Apart from differences in grain size, no difference in either the resulting products nor in their relative amount could be detected in the products resulting from these differently-treated charges. Of three other identical charges to which were added 0.1, 0.25 and 0.5 gm. of sulphur in excess, that with 0.5 gm. additional sulphur blew up, the other two contained the same products and in the same proportions as before, plus sublimated sulphur. Buttons were poorly consolidated and contained some euhedral crystals of stibnite and boulangerite embedded in the sulphur and good needles of stibnite in globules of sulphur which had sublimated in the tubes.

The eutectic of Sb_2S_3 with "mineral X" at 15 per cent PbS by weight is readily prepared; needles of stibnite are first recognizable in fusions containing less than 10 per cent PbS by weight, of "mineral X" in fusions containing more than 20 per cent PbS by weight. The eutectic reported by Iitsuka at 78 per cent PbS could not be duplicated. Three charges of this composition were made up and variously cooled but in each the only phases present were galena in rounded grains and acicular boulangerite.

Table II lists pertinent data for a representative selection of the fusions made. Fusions with subscript 'S' are those in which additional sulphur was charged.

TABLE II.

Fusion No.	Wt. % PbS	Phases Present	Approx. Amts. %*	X-ray Powder Pattern
P7	10.0	1:2	—	—
P8	15.0	1:2	—	—
P5	20.0	1:2	—	—
P9	25.0	1:2	—	—
M1 ($3PbS \cdot 4Sb_2S_3$)	34.5	1:2	40:60	"Mineral X" and strong stibnite lines
M1S ($3PbS \cdot 4Sb_2S_3$)	34.5	1:2	40:60	"Mineral X" and strong stibnite lines
P1	35.0	1:2	40:60	"Mineral X" and strong stibnite lines
P2	40.0	1:2	—	
P11	40.0	1:2:3	25:45:30	
P17	40.0			
M3 ($9PbS \cdot Sb_2S_3$)	41.6	1:2	20:80	"Mineral X" only
M4 ($5PbS \cdot 4Sb_2S_3$)	46.8	1:2:3	5:75:20	"Mineral X" only
P15	47.0			
M5 ($3PbS \cdot 2Sb_2S_3$)	51.3	2:3, trace 1	70:30	"Mineral X" only
M55 ($3PbS \cdot 2Sb_2S_3$)	51.3	2:3, trace 1	70:30	"Mineral X" only
M6 ($5PbS \cdot 3Sb_2S_3$)	53.9	2:3	60:40	"Mineral X" and strong boulangerite lines
M7 ($7PbS \cdot 4Sb_2S_3$)	55.2	2:3	40:60	Boulangerite and "mineral X"
M8 ($2PbS \cdot Sb_2S_3$)	58.2	2:3:4	20:70:10	Boulangerite
M10 ($9PbS \cdot 4Sb_2S_3$)	61.3	3:4	90:10	Boulangerite and strong galena lines
M9 ($5PbS \cdot 2Sb_2S_3$)	63.7	3:4	85:15	Boulangerite and galena
M14 ($3PbS \cdot Sb_2S_3$)	67.9	3:4	80:20	Boulangerite and galena
M11 ($26PbS \cdot 7Sb_2S_3$)	72.3	3:4	75:25	Galena and strong boulangerite lines
M12 ($4PbS \cdot Sb_2S_3$)	73.1	3:4	75:25	Galena and strong boulangerite lines
M13 ($5PbS \cdot Sb_2S_3$)	77.8	3:4	60:40	Galena and strong boulangerite lines

In the above table, Phase 1 = stibnite
Phase 2 = "mineral X"
Phase 3 = boulangerite
Phase 4 = galena

* The approximate percentages of the different phases present are listed in the order corresponding to that in which the phases are listed.

Under "X-ray powder pattern," the phase represented by the dominant lines on the composite photograph is listed first.

Discussion.—Failure to obtain a homogeneous product from any one of the fusions is, possibly, the most notable feature of the results of direct fusion. It is possible that cooling was too rapid to permit maintenance of equilibrium. A more interesting possibility is that sublimation of Sb_2S_3 at temperatures below the freezing point of all products, including the eutectic, is responsible for alteration of some products subsequent to crystallization. This factor was further investigated and will be discussed later in this paper.

It is perhaps surprising that, in view of the differences to be expected in equilibrium between closed and open systems, the results obtained do bear so close a resemblance to those of earlier investigators. The eutectic at 15 per cent PbS by weight is in accord with the results of both Jaeger and Van Klooster and of Iitsuka. Bearing in mind the possibility of loss by sublimation of Sb_2S_3 in an open system, it is possible that the "jamesonite" ($2PbS \cdot Sb_2S_3$) of both previous writers is the equivalent of the boulangerite obtained in this investigation. "Mineral X" prepared in closed system may similarly be the equivalent of the plagionite of Jaeger and Van Klooster and of the warrenite of Iitsuka.

Vapor pressure of sulphur in the presence of its liquid phase is of the order of 6 atmospheres at 600° C (Handbook of Chemistry and Physics, 1933). The fact that neither the presence of sulphur in excess nor the pressure so generated has any appreciable effect on the products of fusion, serves to strengthen the belief that the products reported above are those most stable at the elevated temperatures at which they crystallized. This belief is further corroborated by the fact that wide differences in methods of cooling also had little effect on the resulting products.

SYNTHESIS FROM AQUEOUS SOLUTIONS.

Despite wide divergence of current opinion regarding the genesis of ore deposits, there is a general agreement that most meso-, xeno- and epi-thermal minerals were ultimately deposited from aqueous solutions. In artificial synthesis the principal divergences from postulated natural conditions are the substitution of a closed for an open system and the relatively short time of reaction in the laboratory. Obviously in a closed system equilibrium conditions change rapidly as fractional crystallization takes place whereas in nature the solutions are envisaged as being constantly replenished over relatively great intervals of time.

A paper by Pouget (12) appears to be the only reference to previous work on hydrosynthesis of lead sulphantimonites. Mellor (9) comments that Pouget's products were probably heterogeneous, an opinion corroborated by the writer after duplicating Pouget's methods and taking X-ray powder photographs of the products. None of these products are equivalent to known minerals or to other synthetic lead sulphantimonites. Several references to analogous hydrosynthesis of silver sulphantimonites have been summarized by Béland (1), who concludes that such sulpho-salts can be crystallized only from alkaline solutions and most readily from alkaline sulphide solutions.

Method and Materials.—Hydrosyntheses were carried out in a steel crucible lined with graphite. This crucible was designed by Dr. F. G. Smith of the University of Toronto to whom the writer is indebted both for drawings of it and for assistance in the technique of its use.

The crucible was heated in a well-insulated electric furnace. Since the heat capacity of the charge is small relative to the heat capacity of the crucible, the temperature of the charge is assumed to be the same as that of the crucible. The latter is measured by a thermocouple whose hot end fits into a hole drilled into the base of the crucible.

Temperatures to which the charges were subjected ranged from 200° C to a maximum of 435° C. Equivalent pressures are estimated from a graph compiled by Béland (1), in which curves pass through points for which the specific volume of water is the same. The specific volume and temperature of the charge being known, the pressure may be read off directly. Maximum estimated pressures varied up to 2,200 bars.

Reagents are charged together in the crucible. Where, however, reaction between them is rapid (as between acids and bases), temporary segregation was effected by charging one such reagent in an inner graphite crucible with

TABLE III.

BR No.	$Na_2S \cdot 9H_2O$	S	Addit. H_2O	Pb	$PbCl_2$	Sb	Other	Max. Temp.	Total Time	Products	
										Solution	Solids (in approx. order of amount)
1	19.5	13.0	24.5	2.0	—	6.0	—	395°C	72½ hrs.	Alk.	Lead, stibnite, sulphur, trace galena.
2	—	2.3	37.0	1.5	—	2.3	6.0 CaS	360	72½ hrs.	Alk.	Lead, antimony, little antimony, little sulphur.
3	19.5	13.0	28.5	2.0	—	2.0	—	380	73½ hrs.	Alk.	Lead, stibnite, sulphur, little galena, trace semseyite (?).
4	19.5	13.0	24.5	6.0	—	2.0	—	340	87½ hrs.	Alk.	Stibnite, lead, sulphur, little galena, trace semseyite.
5	39.0	10.0	17.0	6.0	—	2.0	—	370	76 hrs.	Alk.	Lead, galena, sulphur, stibnite antimony.
6	19.5	5.0	32.5	6.0	—	2.0	—	380	86 hrs.	Alk.	Lead, galena, stibnite, antimony.
7	10.0	13.0	38.0	6.0	—	2.0	—	370	79 hrs.	Alk.	Stibnite, lead, sulphur, galena, little semseyite.
8	39.0	25.0	14.0	6.0	—	2.0	—	365	76½ hrs.	Alk.	Sulphur, galena, semseyite, little stibnite, little lead, brown felted mass.
9	25.0	20.0	20.0	2.0	—	12.0	—	375	77 hrs.	Alk. (gelatinous)	Stibnite, sulphur, galena, little lead, few fuloppite xals.
10	12.0	10.0	7.0	0.35	—	6.0	—	380	47 hrs.	Nil	Stibnite, lead, trace fuloppite.
11	15.0	15.0	15.0	2.0	—	6.0	5.0 NaOH	360	72 hrs.	Alk.	Stibnite, galena, fuloppite, sulphur, lead.
12	12.0	15.0	14.0	—	4.0	3.0	—	360	70 hrs.	Alk.	Sulphur, plagionite, galena, little stibnite, matted red hairs (Sb_2S_5?).
13	15.0	15.0	15.0	3.0	—	4.0	5.0 NaOH	370	57½ hrs.	Alk.	Sulphur, lead, stibnite, fuloppite coating lead.
14	12.0	15.0	14.0	—	5.0	3.0	—	375	52½ hrs.	Alk.	Much sulphur, plagionite, stibnite, galena, zinkenite.
15	10.0	10.0	20.0	—	—	2.0	4.6 PbS; 5.0 NaOH	385	120 hrs.	Alk.	Sulphur, semseyite, stibnite (stubby xals), little galena.
16	10.0	10.0	20.0	—	6.0	—	2.0 $SbCl_3$	370	53 hrs.	Alk.	Galena, sulphur, semseyite, "Mineral X," no stibnite.
17	10.0	10.0	20.0	—	6.0	—	2.0 $SbCl_3$	215	98 hrs.	Alk.	Sulphur, galena, red ppt. of Sb_2S_5.
18	10.0	10.0	20.0	—	6.0	—	3.0 PbS; 5.0 $SbCl_3$; 5.0 HCl	220	69 hrs.	Acid	Sulphur, stibnite, lead apparently in solution.
19	10.0	10.0	15.0	—	4.0	—	4.0 PbS; 4.0 $SbCl_3$; 5.0 HCl	390	82 hrs.	Acid	Stibnite, galena, matted red Sb_2S_5, little "mineral X," little fuloppite, trace sulphur.
20	15.0	10.0	15.0	—	—	—	10.0 PbS; 5.0 $SbCl_3$; 5.0 HCl	355	96 hrs.	Neutral	Stibnite, galena, little sulphur, trace semseyite.
21	8.0	10.0	10.0	—	4.0	0.5	—	365	94 hrs.	Alk.	Semseyite, sulphur, Phase I, galena.
22	4.0	5.0	20.0	—	2.0	—	$9PbS \cdot 4Sb_2S_3$ 0.2	350	34 hrs.	Alk.	Semseyite, galena, little sulphur.
23	15.0	15.0	15.0	—	6.0	1.0	NaOH 5.0	350	57 hrs.	Alk.	Semseyite, galena, stibnite, sulphur.
24	5.0	5.0	20.0	—	8.0	1.0	—	350	92 hrs.	W. alk.	Galena, zinkenite, little stibnite, little semseyite, little sulphur, trace $PbCl_2$.

TABLE III—*Continued.*

BR No.	$Na_2S \cdot 9H_2O$	S	Addit. H_2O	Pb	$PbCl_2$	Sb	Other	Max. Temp.	Total Time	Products	
										Solution	Solids (in approx. order of amount)
25	—	5.0	15.0	—	6.0	1.0	HCl 10.0; FeS 10.0; —	290	87½ hrs.	Acid	Galena, $PbCl_2$, stibnite, pyrite, some sulphur.
26	8.0	10.0	10.0	—	6.0	1.0	FeS 5.0; — ; —	375	72 hrs.	Alk.	Semseyite, galena, $PbCl_2$, zinkenite, Sb_2S_3, pyrite, some sulphur.
27	8.0	10.0	11.0	—	2.0	0.5	— ; — ; —	365	95 hrs.	Alk.	Semseyite, galena, little zinkenite, very little "mineral X," some $PbCl_2$, Sb_2S_3.
28	8.0	10.0	10.0	1.5	—	0.25	8.0 $NaHCO_3$; — ; —	325	72 hrs.	Alk.	Sulphur, lead, galena.
29	15.0	10.0	10.0	—	2.0	0.25	5.0 NaCl; — ; —	400	74 hrs.	Alk.	Zinkenite, sulphur, galena, semseyite, little "mineral X."
30	—	15.0	10.0	—	—	1.0	4.0 $PbNO_3$; 10.0 K_2S; —	385	52 hrs.	Alk.	Stibnite, semseyite, galena, sulphur, some zinkenite.
31	6.0	7.5	7.0	—	2.0	1.0	— ; — ; —	395	74 hrs.	Alk.	Mineral X, felted acid xals, plagionite, galena, $PbCl_2$, little sulphur.
32	—	12.0	8.0	—	—	—	1.4 PbS; 0.75 Sb_2S_3; 12.0 K_2S	395	71 hrs.	Nil	Sulphur, galena, Phase I.
33	8.0	1.5	9.0	—	4.0	1.0	— ; — ; —	360	68 hrs.	Alk.	Semseyite, galena, Phase I, stibnite, trace sulphur.
34	15.0	10.0	10.0	—	2.0	0.25	10.0 Na_2CO_3; — ; —	375	78 hrs.	Alk.	Galena, recrystallized Na_2CO_3, much sulphur.
35	6.0	7.5	7.0	—	—	—	$5PbS \cdot 2Sb_2S_3$ 1.0	355	54 hrs.	Alk.	Unaltered fragments of boulangerite, sulphur, brown acic xals.
36	40.0	—	—	—	—	—	4.0 PbS; 1.0 Sb_2S_3; —	425	91 hrs.	Alk. (colorless)	Phase III, no sulphur, orange ppt. soluble in water.
37	40.0	18.0	—	—	—	—	4.0 PbS; 1.0 Sb_2S_3; —	410	70 hrs.	Alk. (green)	Phase III, sulphur, some galena.
38	15.0	10.0	10.0	—	2.0	0.25	15.0 NaCl; — ; —	420	118 hrs.	Alk.	Very fine grained Phase II, intergrown with galena, some sulphur.
39	5.0	5.0	20.0	—	8.0	1.0	0.5 Ag; — ; —	365	120 hrs.	Alk.	Galena, zinkenite, semseyite, pyrargyrite, acanthite, andorite, equant silver sulphantimonite.
40	7.5	7.5	10.0	—	—	0.5	2.0 PbS; 5.0 NaOH; —	430	68 hrs.	Alk.	Phase III, little galena, trace stibnite.
41	—	10.0	10.0	—	—	0.5	2.0 PbS; 20.0 CaS; —	438	93 hrs.	Alk.	Stibnite, residual CaS, galena.
42	15.0	10.0	15.0	—	—	0.5	2.5 PbS; 5.0 H_2SO_4; —	380	75 hrs.	Neutral	Galena, zinkenite, sulphur.
43	5.0	10.0	13.0	—	2.0	0.25	15.0 NaCl; — ; —	415	92 hrs.	Alk.	NaCl, $PbCl_2$, fuloppite, galena, "mineral X," Phase I, stibnite, sulphur.
44	5.0	5.0	15.0	—	2.0	0.25	25.0 NaCl; — ; —	435	192 hrs.	Alk.	NaCl, galena, stibnite, fuloppite, Phase I, some sulphur, little $PbCl_2$.

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a screw top. On heating, permeability of the graphite permits passage of the reagents through it.

Charges were brought to a maximum temperature over a period of 24 hours and cooled to room temperature over intervals ranging from two to ten days. Products were washed out with distilled water and examined under the binocular microscope, where they were segregated for X-ray powder and single crystal photographs, for determination of specific gravity, etc.

Solvents used in alkaline runs were $Na_2S \cdot 9H_2O$, K_2S, and CaS with varying amounts of sulphur. For acid runs, HCl was charged with either sulphur or FeS. Lead and antimony were variously charged as pure metals, as chlorides and, in some instances, as sulphides. The effects on yield of lead sulphantimonites of Cl^-, HCO_3^- and $CO_3^=$ ions were evaluated by addition of NaCl, $NaHCO_3$ and Na_2CO_3 respectively.

Results of Hydrosynthesis.—Table III lists the charges, maximum temperatures, and total time of heating and cooling of the 44 experiments made. Charge BR39 was used to determine whether the more complex lead-silver sulphantimonites could be prepared under similar conditions.

Solid products of hydrosynthesis usually form a mass in the bottom of the crucible. Single crystals rarely exceed 2 mm in greatest dimension; the great majority are much smaller. The following products, produced in various experiments, are listed in order of readiness of crystallization from the aqueous solutions employed:

(1) Galena PbS
(2) Stibnite Sb_2S_3
(3) Fuloppite $3PbS \cdot 4Sb_2S_3$
(4) Plagionite $5PbS \cdot 4Sb_2S_3$
(5) Semseyite $9PbS \cdot 4Sb_2S_3$
(6) Zinkenite $PbS \cdot Sb_2S_3$
(7) Mineral X $7PbS \cdot 6Sb_2S_3$
(8) Phase I $6PbS \cdot Sb_2S_3$
(9) Phase III $Na_2S \cdot 2Sb_2S_3$
(10) Phase II $5PbS \cdot 4Sb_2S_3$

CONDITIONS OF FORMATION OF THE DIFFERENT PRODUCTS.

Plagionite Group Minerals.—Lead sulphantimonites of this group, relatively rare as minerals, were the most readily-crystallized sulphosalts in hydrosynthesis. Their maximum yield occurs under moderately high alkaline concentrations, although traces of fuloppite were detected in BR No. 19 whose residual solution proved acid to litmus. Addition of NaOH increases deposition of this group but in the presence of NaCl the yield is diminished. $NaHCO_3$ and Na_2CO_3 when added to the solutions sharply decrease formation of all sulphantimonites. Never more than one member of the group is found among the products of any one experiment; the member crystallizing is determined by the relative concentration of lead and antimony in solution.

Acicular Lead Sulphantimonites.—This group includes zinkenite, "mineral X," and Phases I and II. More than one of these compounds was recognized in several bomb runs. They form most readily in relatively dilute alkaline solutions but no member of this group was found in acid runs. In contrast to the plagionite group, NaCl increases yield of these minerals and NaOH decreases it. Phase II was precipitated in BR No. 38 only, where concentration of NaCl was at its maximum.

Phase III.—This product develops only under the extremely alkaline conditions of BR Nos. 36, 37 and 40. In these runs, what little lead was deposited was in the form of galena; the greater amount remained in solution. Phase III formed the large majority of the solid products and in it sodium is deposited instead of lead as a sulphantimonite. It is worthy of note that sulphur concentration has little effect on crystallization as indicated by similarity in products of BR Nos. 36 and 37.

Galena.—Galena occurs equally readily as a product of both acid and alkaline solutions. Its absence in BR Nos. 18 and 36, however, indicates that it is soluble in very concentrated acid or alkaline solutions. It was noted forming by replacement of crystals of $PbCl_2$; elsewhere it is the first product to crystallize. Development of galena is somewhat reduced by addition of NaCl.

Stibnite.—Like galena, stibnite is formed equally readily in acid and alkaline solutions. Although it is not precipitated from highly alkaline solutions, best development of stibnite crystals took place in BR No. 18 in which pH values were lowest. Yield of stibnite is little affected by addition of NaOH but is reduced in the presence of NaCl when optimum conditions for formation of the acicular lead sulphantimonites prevail.

ORDER OF CRYSTALLIZATION.

In polished sections of artificial products, semseyite may be seen forming by replacement of galena whereas fuloppite forms directly on metallic lead or as single crystals. Sheaves of zinkenite have been observed growing directly on faces of semseyite. Nearly all products have been observed growing on "shells" and aggregates of galena. Apart from these direct observations, paragenesis rests on spatial relationships within the crucible. Order of crystallization from earliest to latest is: galena, long and overlapping; plagionite group minerals; acicular lead sulphantimonites and stibnite.

EFFECTS OF DIFFERENT FACTORS ON SYNTHESIS.

In any closed system it is obvious that equilibrium conditions are constantly changing as various products crystallize; it is possible only to reason from such factors as the original charge, the conditions of temperature and pressure, the order of crystallization and the final products derived.

Although 44 experiments were made in attempts to synthesize the various lead sulphantimonites from aqueous solutions, due to the large number of factors involved, a very much larger number of experiments would be necessary to evaluate unequivocally the effects of each variable. Perhaps the most difficult factor to control is the solubility of lead. Certainly charging metallic lead is unsatisfactory due to the difficulty of getting it into solution. Charging lead as galena does correspond more nearly to natural conditions, since all indications point to the fact that galena, generally, is deposited before, and is replaced by the lead sulpho-salts. There is much natural evidence supporting the use of $PbCl_2$ in the charge; certainly this lead salt is more soluble than any other for which there is such justification. In discussing effects of the

different factors, the form in which lead was charged must be considered as an over-riding control.

Lead Charged as Metallic Pb.—Lead was so charged in Nos. 1–11 inclusive, 13 and 28. As most experiments were conducted above the melting point of lead, there was a slight tendency for the finely granulated powder to coalesce and to form globules in which the surface presented to solutions was at a minimum. Lead was taken into solution in appreciable amount only in the presence of high concentrations of Na_2S and sulphur (high concentration of Na_2S with little sulphur was relatively ineffective) and in lower concentrations of Na_2S fortified by NaOH in presence of excess sulphur (Nos. 11 and 13). Thus in order to bring the lead into solution, highly concentrated solutions were required. From these solutions the only sulphantimonites precipitated were fuloppite and semseyite, together with galena and stibnite. It may be reiterated that whereas in No. 8 semseyite formed by replacement of galena, in No. 11, and particularly in No. 13 fuloppite formed directly on the lead and to a lesser extent as single crystals.

Lead Charged as PbS.—Lead was so charged in Nos. 15, 18, 19 (in part), 20, 36, 37, 40, 41, 42. This was done in attempts to synthesize boulangerite by replacement of galena. Galena is apparently readily soluble in strongly alkaline solutions (Nos. 15, 36, 37 and 40) and in acid solutions (No. 18), but not in weakly alkaline nor in concentrated but nearly neutral solutions. This is in contrast to antimony which is readily precipitated from acid and strongly alkaline solutions but is more soluble in dilute and neutral solutions.

Lead Charged as $PbCl_2$.—Lead was so charged in Nos. 12, 14, 16, 17, 19 (in part), 21–27 (incl.), 29, 31, 33, 34, 38, 39, 43 and 44. Only when charged in this form was it possible to determine the sulpho-salt yield from relatively dilute alkaline solutions.

Effect of Pb: Sb Ratio.—The effective ratio of lead and antimony in solution is controlled by (a) the form in which lead is charged and (b) the amount of galena which has separated at the time of sulpho-salt formation. The effect of the Pb:Sb ratio is: less than 1:1 fuloppite forms, between 1:1 and 2:1 plagionite forms, greater than 2:1 semseyite forms. The effective Pb:Sb ratio is much more difficult to assess at the time of deposition of the acicular products which appear to form after members of the plagionite group. In general, however, a high ratio is associated with formation of Phase I (Nos. 43 and 44 within the inner tube and Nos. 21 and 33), possibly not quite so high a ratio with Phase II, and relatively lower ratios with "mineral X" and zinkenite.

Effect of $S^=$ Ion Concentration.—Reference has been made to the effect of additional sulphur in effecting solution of lead (Nos. 5 and 8). Quite clearly increase in the $S^=$ ion concentration increases the solubility of lead in concentrated Na_2S solutions. The effect on yield of sulpho-salts where lead is charged as the chloride is less marked. This is illustrated by Nos. 27 and 33, the products of which were very similar. In yield of Phase III from Nos. 36 and 37 no marked difference due to difference in sulphur charged was noted.

Effect of Chloride Ion Concentration.—In most cases as noted above, lead was charged as the chloride. To increase the chlorine ion concentration NaCl

was charged in some instances. Obviously other charges containing HCl and $SbCl_3$ were also high in chlorine, but in these the addition of chlorine affected the hydrogen-ion concentration also. NaCl was charged in Nos. 29, 38, 43 and 44. As noted earlier, best yields of zinkenite were obtained from relatively dilute Na_2S solutions. Comparing the products of runs 21 and 27 with those of 29 in which NaCl was charged suggests that increased chlorine ion concentration has the effect of increasing the yield of zinkenite and decreasing the yield of semseyite. No. 38 with three times the NaCl content of No. 29 yielded large quantities of Phase II (an acicular mineral) and no semseyite. In Nos. 43 and 44, the inner graphite tube prevented the attainment of equilibrium; hence their products cannot be used for comparison. The general effect then of addition of a neutral chloride is to increase yield of the acicular group of products and to decrease that of the plagionite group. A second, but less pronounced, effect is shown in a decrease in amount of galena precipitated with a corresponding increase in the percentage of lead deposited as a sulphantimonite.

Effect of Na_2CO_3 and $NaHCO_3$.—The effect of Na_2CO_3 in repressing formation of sulphantimonites is clearly brought out by comparison of Nos. 29 and 34. Charges were identical except that in No. 29 NaCl was charged and in No. 34 Na_2CO_3. No. 34 contained galena only; the antimony remained in solution. No sulphosalts were formed. $NaHCO_3$ was charged in No. 28 in which metallic lead was also charged. The charge containing no $NaHCO_3$ and most nearly similar otherwise is No. 7; the main additional difference being the relatively low concentration of Na_2S in No. 7. In the charge containing $NaHCO_3$, lead and galena were metallic products, antimony remained in solution; without $NaHCO_3$ antimony was precipitated as stibnite and some semseyite was formed. The effects of both Na_2CO_3 and $NaHCO_3$, therefore, are (a) to repress formation of sulphantimonites and (b) to increase solubility of antimony.

Effect of Hydrogen Ion Concentration.—Firstly, low pH values increase solubility of lead and decrease solubility of antimony in the presence of high concentration of sulphur and sodium (Nos. 18, 19). Solubility of neither lead nor antimony is enhanced by low pH values in the absence of Na and with low S ion concentration (No. 25). Generally, low pH values decrease the yield of sulphantimonites; these were found in very small amount only in No. 19, which contained double the amount of lead that was charged in No. 18. Very high pH values (Nos. 36, 37 and 40) increase the solubility of lead to a marked degree but do not increase solubility of antimony. High pH values repress formation of lead sulphantimonites. Greatest yield of members of the plagionite group was obtained in No. 21 in which pH values were moderately high. Greatest yield of acicular lead sulphantimonites (in solutions free from NaCl) was obtained from No. 24, a solution in which alkalinity was relatively low.

Effect of Maximum Temperature.—Most experiments were carried out at relatively high temperatures (circa 400° C.) in order to expedite reactions. In order to verify the assumption that high temperature does in fact have such an effect, No. 17 with the same charge as No. 16 was heated at 215° C for

almost twice the length of time employed in heating No. 16. No sulphantimonites were precipitated at the lower temperature but galena and stibnite formed readily. Thus high temperatures promote formation of lead sulphantimonites from aqueous solutions.

Effect of Time.—To offset in the laboratory the tremendous time intervals available in nature for nuclear formation, recourse has been taken to both higher temperatures and more concentrated solutions than are to be expected under natural conditions. In Nos. 43 and 44 charges were very similar. The addition of NaCl in No. 44 was ineffective as solution was almost certainly supersaturated in No. 43. No. 44 was held above 400° C more than twice as long as No. 43. Resultant galena development was almost twice as great as in No. 43. Nos. 9 and 10 were also similar in charge but in No. 9 quantities were charged in almost double the amount of No. 10. Here pressure and time were the two factors varied. Far less reaction took place in the shorter time (and at lower pressure) at which No. 10 was heated. Increasing time of heating does therefore tend to increase reaction.

Effect of Pressure.—Comparison has been made above between Nos. 9 and 10 in which pressures developed differed considerably and in which greater reaction took place at higher pressure, but also on longer heating. Comparison of Nos. 27 (greater pressure) and 31 (lower pressure) indicates that a greater yield of lead sulphantimonite accompanied the lower pressure, shorter time and greater concentration of antimony. Hence effect of pressure (and to a lesser extent of time) cannot be satisfactorily evaluated.

Effect of Total Metal Concentration.—A comparison of Nos. 12 and 14 with Nos. 27 and 31 indicates that a slightly higher relative yield of lead sulphantimonites was obtained where the total metal to solvent ratio was low. This effect is not as pronounced as might be expected due partly to the difference in solubility of lead and antimony. Where relatively little antimony is charged, there is a tendency for it to remain in solution.

Effect of Different Solvents.—The three alkaline sulphides used in aqueous solution were Na_2S, K_2S and CaS. Runs No. 2 and 41 show that CaS is relatively ineffective as a solvent. K_2S and Na_2S appear to be equally effective as solvents.

EFFECTS OF HEATING PRODUCTS OF HYDROSYNTHESIS IN A VACUUM.

In comparing products of hydrosynthesis with those of direct fusion, it is remarkable that only "mineral X," a mineral known from only one locality in nature, should be a product of both methods of synthesis; while boulangerite, the most common of the natural sulphantimonites, is a product of direct fusion only. Since sublimation of Sb_2S_3 on the walls of the tubes was a notable feature of direct fusion, it seemed that this factor might be the reason for the non-appearance of other lead sulphantimonites. Earlier work by Hawley (1941) and Tarry (1945) in the Cu-Fe-S system had indicated that marked mineral transformations do occur on heating in the solid state. Products of hydrosynthesis were therefore heated in a vacuum at temperatures below that of the eutectic in the PbS-Sb_2S_3 system.

Clean single crystals from various hydrosyntheses were sealed in evacuated glass tubes and heated at a temperature of 415° C plus or minus 10° C for periods up to 12 days. The products were examined before and after heating in polished section and identified by X-ray powder photographs. Table IV shows the products charged and the results of heating them. As alteration was incomplete in some cases, the degree of alteration is estimated by the dominating X-ray powder pattern and the strength of lines in the subsidiary pattern.

TABLE IV.

Product	Formula	Time	Resulting Product	Formula
1. Fuloppite	$3PbS \cdot 4Sb_2S_3$	12 days	"Mineral X"—trace fulop-pite.	($7PbS \cdot 6Sb_2S_3$ approx.)
2. Zinkenite	$PbS \cdot Sb_2S_3$	12 days	"Mineral X"—trace zink-enite.	($7PbS \cdot 6Sb_2S_3$ approx.)
3. Plagionite	$5PbS \cdot 4Sb_2S_3$	12 days	Boulangerite—trace plagionite.	($5PbS \cdot 2Sb_2S_3$)
4. Semseyite	$9PbS \cdot 4Sb_2S_3$	12 days	Semseyite—trace boulangerite.	
5. Semseyite	$9PbS \cdot 4Sb_2S_3$	6 days	Semseyite—some boulangerite.	
6. Semseyite	$9PbS \cdot 4Sb_2S_3$	12 days	Semseyite and boulan-gerite (equal).	
7. Semseyite—galena	$9PbS \cdot 4Sb_2S_3$	12 days	Boulangerite only.	
8. Phase I	$6PbS \cdot Sb_2S_3$	12 days	Galena trace (?).	(PbS)
9. Phase II	$5PbS \cdot 4Sb_2S_3$	12 days	Unknown.	

In all cases where single crystals were charged, they were unchanged in form and their lustre undiminished after heating. In some instances up to 25 per cent of the crystals had broken. In all cases where a single product was charged a fine film of brown sublimate was observed on the walls of the tube, which corresponded approximately to the amount of Sb_2S_3 lost in the alteration. Where powdered semseyite and galena were charged in proportions equivalent to the composition of boulangerite, no film was observed. In polished section the alteration could be observed under polarized light; the uniform polarization colors of the single crystals are replaced by wavy subparallel bands of varying colors due to varying orientation of very fine grained acicular crystals.

DISCUSSION.

Alteration of products of hydrosynthesis by heating in the solid state invariably involves loss of Sb_2S_3 by sublimation. The residual solid product is always one of those which was found to be stable under conditions of direct fusion. Further, the resulting stable product is always that one which contains a higher percentage of PbS than, and which is nearest in composition to, the original material being heated. For example, zinkenite alters to "mineral X," not to boulangerite. Finally it is indicated that some reaction can occur between the sublimated Sb_2S_3 and galena to form boulangerite.

SUMMARY AND CONCLUSIONS.

Products of direct fusion of PbS and Sb_2S_3 in a closed evacuated system appear to be unchanged by the addition of excess sulphur. Where sulphur in excess is added, its solidification within the melt detracts from the consolidation of the latter but tends to promote euhedral crystallization of the acicular phases. Stibnite in small euhedral crystals is also found in globules of sulphur at the top of the tube. Other products are galena, boulangerite and "mineral X." The two lead sulphantimonites are probably the equivalents of the two reported by Jaeger and Van Klooster as plagionite and jamesonite and of two of the four reported by Iitsuka. Migration of Sb_2S_3 observed in direct fusion and corroborated by results of heating other lead sulphantimonites in a vacuum has received little attention by these two previous workers, both of whom worked, apparently, with an open system. Iitsuka, however, does not describe conditions under which his fusions were made; it is possible that under high containing pressures, other lead sulphantimonites might be stable. There would appear to be little likelihood that natural lead sulphantimonites are ever deposited under conditions equivalent to those employed in direct fusion.

Products of synthesis from various aqueous solutions may be divided into three groups: first, the end products galena and stibnite, secondly, the tabular lead sulphantimonites of the plagionite group, fuloppite, plagionite and semseyite, and finally the acicular lead sulphantimonites, zinkenite, "mineral X" and Phases I and II. Of these, the first group crystallize under a very wide range of conditions, the second dominantly from moderately concentrated alkaline sulphide solutions and the third from more dilute alkaline sulphide solutions, their yield being enhanced by addition of NaCl.

Absence of boulangerite, the most common natural sulphantimonite in hydrosynthesis, is remarkable. Its stability in solutions used in hydrosynthesis was demonstrated in BR No. 35. By contrast the plagionite group, among the rarest natural sulphantimonites, are relatively readily synthesized from the solutions used, whereas the commoner natural mineral, zinkenite, is less readily synthesized. These reversals of natural occurrence are probably due, largely, to departures in the laboratory from postulated natural conditions of temperature, pressure and concentration. Deposition of the acicular group and stibnite in the bomb is demonstrably later than that of the plagionite group; deposition of galena is long and overlapping. It would thus appear that lowered temperature and pressure and/or lowered metal concentration in solution favor deposition of the more common minerals. Unfortunately the time of reaction under such conditions would be distinctly increased and due to this time factor the writer has not been in a position to verify this hypothesis. The generally slower nuclear formation of more stable, as contrasted to less stable, compounds is linked to this hypothesis in the case of boulangerite; thus it is quite possible that this mineral could be synthesized under conditions modified as suggested above, given adequate time.

Justification for the use, primarily, of alkaline sulphides as solvents may be found in their ability to transport gold (15) and in their presence in the

two best known hot springs currently depositing sulphides, those of Steamboat Springs, Nevada, and Aix-les-Bains, Vosges, France. NaCl, too, is a very common salt in hot springs and in concentrated solution is the most common salt of liquid inclusions of sulphides, of the Tri-state field and elsewhere. Na_2CO_3 and $NaHCO_3$ are also very common salts in hot springs but their concentration at the surface relative to that in the zone of mineral deposition is not known.

Primary results of these hydro-syntheses are that optimum conditions for formation of lead sulphantimonites include:

Alkaline sulphide solutions
Presence of NaCl
Relatively low metal to solution ratios

Further, yields are increased by increases in time of reaction, temperature of reaction and, to a lesser degree, of pressure.

Alteration of most sulphantimonites, crystallized originally from aqueous solution, to others stable under conditions of direct fusion, by loss of Sb_2S_3 when heated below their melting points in a vacuum has been demonstrated. The effect of increasing pressures and reducing temperatures beyond those used has not been investigated. Mead (8) has shown that deformation of a potentially dilatant mass causes a decrease in pressure of the fluid portion; such a factor might produce conditions of lowered pressure in nature, thus favoring this type of alteration. Requisite temperatures for such alterations may be supplied by residual heat or by an advancing thermal gradient due to subsequent intrusion of igneous rocks or their apophyses.

Although alteration of other lead sulphantimonites to boulangerite and "mineral X" under conditions of elevated temperature has been demonstrated, there are no indications of alteration taking place in the reverse direction. Thus these two compounds would be expected to be more stable in nature than the others. There is, however, only one known natural occurrence of "mineral X" whereas boulangerite is a relatively common mineral. The possibility that "mineral X" is a metastable phase is thus presented; there is, however, no evidence in the natural material for any tendency for it to alter other than by oxidation and hydration to bindheimite.

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REPORT OF COMMITTEE ON RESEARCH IN ENGINEERING GEOLOGY, SOCIETY OF ECONOMIC GEOLOGISTS.[1]

SIDNEY PAIGE AND ROGER RHOADES.

INTRODUCTION.

SIDNEY PAIGE.

BEFORE discussing research in "Engineering Geology," some simple definitions may be offered.

Engineering, and particularly civil engineering, is that field wherein men cultivate and apply the basic sciences to accomplish better desirable social objectives—to build dams, roads, ditches, embankments, tunnels, foundations.

Geology on the other hand concerns the anatomy and nature of the earth and its envelope—the atmosphere, its origin and evolution, the physics and chemistry and mechanics that underlie the processes that have affected it in the past, and are operating today—of which there are legion.

Since engineering projects, particularly large ones, involve changes in the surface of the earth, take advantage of the configuration of the earth, disturb one way or another processes active in the earth, set up stresses that result in strain, of one kind or another, engineers turn naturally to geologists for advice in order that their works may be stabilized, operate satisfactorily, and be called good.

Research is the search for new knowledge. Throughout the years, especially during the last three centuries, immense and specialized fields of systematized knowledge have been built up—evolved—and now constitute the broad framework of science as we know it. And all of this has been accomplished because of a "point of view," a slant in thinking, the recognition of cause and effect, the concept of the measured unit quantity, the possibility of the predicted result—in a word, the scientific method.

When therefore, we speak of progress of research in engineering geology, we really mean progress in the application of geologic principle to engineering needs—progress in understanding by geologists of engineering principles—progress in cooperation, and a sharpened understanding between the two fields of enquiry.

Naturally, responsibility for progress rests on both engineers and geologists. Principles and practice go hand in hand. One without the other limps. This has always been so, although not recognized in the past as it is today, and from this recognition has grown the imperative need for the point of view of the engineering geologist.

[1] This is the sixth of a series of reports under "Committee on Research," Society of Economic Geologists, Charles H. Behre, Chairman.

In the past disaster has followed failure to recognize this need. Today disaster or frustration still impends, where groups of men fail to keep abreast of developments, and promote projects, the implications of which they do not understand.

Dr. Rhoades, burdened with many other duties, as were his associates, has been at great pains to assemble and present the clear exposition that follows, of the field as it moves forward today. Among the generous contributors of their time are B. C. Moneymaker, Allen S. Cary, Arthur Bevan, Henrich Ries, Charles P. Berkey, A. B. Cleaves, R. F. Legget, E. B. Burwell, E. B. Eckel, Stafford Happ, Ross Heaton, Carl Heiland, W. H. Irwin, and Shailer S. Philbrick.

There is hardly a field of research in geology which will not ultimately be used in the approach to perfection that is the ideal of the civil engineering profession.

Time has not permitted all of the above individuals to read this report prior to its publication. Accordingly the writers wish to acknowledge gratefully the indispensable assistance of these individuals, but to assume full responsibility for the statements and viewpoints expressed herein, as well as any inadvertent omissions.

It is planned to report annually in this same place a review of progress.

We are all grateful to Dr. Charles H. Behre, Jr., whose broad point of view and inspiration is responsible for this work, a part only of a broader program covering research and the application of geology to various branches of engineering.

ENGINEERING GEOLOGY.

Roger Rhoades and Associates.

By Engineering Geology is meant geology applied to Civil Engineering, as in the investigation, design, construction, or maintenance of such engineering works as dams, tunnels, canals, roads, buildings, powerhouses, or pumping plants, together with the geologic aspects of the investigation, testing, selection, and use of the natural construction materials of which such structures are built. Engineering Geology in this sense is not new, but only in recent years has it become recognized as a distinct field of geological specialization. The field is not yet as formalized as that of Mining Geology or Petroleum Geology; the scope and the content of Engineering Geology are only now approaching precise definition. It has become increasingly evident in the past decade where the geologist fits into an engineering organization, the kind of contribution he can make to engineering enterprises, the extent of his responsibility, and the proper relationship and division of labor between geologists and engineers. These matters are being further clarified. Any geological work related to an engineering undertaking, if it contributes to a better general understanding of the field, can be considered as research; and for the purposes of this report, research has been so defined.

The slow but steady progress in the application of geology to Civil Engineering through the first three decades of this century was sharply accelerated

during the few years immediately preceding the war. This acceleration was maintained during the war, although with the special viewpoints of Military Engineering primarily in mind, notably by the Military Geology units of the United States Geological Survey, but also by parallel organizations in Canada. Further accelerations have occurred in the post-war years as a consequence of the revived and expanded programs of civil works. Today Federal, State and Municipal agencies are utilizing Engineering Geology, as never before, private geologists are entering the field in increasing numbers, and universities and colleges are taking increasing notice of the demand for geologists trained in this special field. Thus, today a very large number of geologists are fully or partially preoccupied with Engineering Geology. The field ranges from simple routines through all degrees of special studies and experimentation, and includes pure research in basic geology and the related fundamental sciences.

Engineering Geology has not yet attained its full maturity. To achieve it and full development, three things will be necessary: first, the development of concepts and techniques for a more quantitative solution of geologic problems; second, a mechanism for more adequate training of geologists in the specific applications of geology to engineering; third, an expanded recognition by both engineers and geologists of engineering geology as an independent professional field. Although all three of these requirements bear upon the interests of this committee, our first concern lies in the development of concepts and techniques permitting more quantitative solutions of the geologic problems with which the engineer is confronted. Geology in general has become steadily more quantitative through research, but the special needs of engineering geology are urgently pressing. Engineers are concerned less with the origins and compositions of rocks, soils, and landscapes, than with their actual physical behavior under the conditions imposed by engineering structures—less with textures, structures and the manners of formation than with strengths, durabilities, settlements, elasticities, compressibilities, unrelieved inherited stresses, structural stability under loading, ability to stand permanently when excavated to a given slope, permeabilities under the new conditions imposed by the construction of a dam or canal. The engineer needs to know these and many other things in closely quantitative terms before he can design and build his structures rationally and confidently. The answers to such questions are too often beyond our present techniques or knowledge. This is a challenge to the geological profession to initiate research discriminately directed toward the development of new concepts and techniques, or the more effective application of those presently available.

Before appraising the progress and objectives of research in engineering geology, it will be well to define in some general way the scope and content of the field. The basis of engineering geology lies in the fact that most engineering structures are built on rock or soil foundations and constructed of rock and soil materials. The geological conditions and materials at any construction site define the natural environment to which the structure must be adapted by the designing and construction engineer; and the safety, economy, and effectiveness of a structure can be gaged in large measure by the appropriate-

ness with which it has been adapted to the peculiar conditions of its particular site. It is the function of the geologist to interpret these natural conditions as quantitatively as possible, in terms of their engineering implications, and with such lucidity that the engineer can design and build the best adapted and most appropriate structure. The need for this kind of geological service becomes greater year by year, as we design increasingly larger and more complex structures and adapt them to poorer and poorer sites. There are literally dozens of large and complex projects on the designing boards today which are proposed for construction at sites which only a decade ago would have been unacceptable. That such projects can be designed and built today is a tribute to the progress which has been made in site investigation and interpretation; but if the trend is to continue, the geological profession must keep pace through research with the increasing demands of the engineering profession.

Proceeding from these general considerations it may be said to be the aim and objective of engineering geology: to engage in those fields in which the objective of an engineering undertaking can be furthered by the applications of geological principles; to improve and extend the translation of geological findings into conclusions of direct engineering usefulness; to encourage and prosecute research toward a more complete and more quantitative interpretation of geological phenomena and principles in terms of their engineering significance, and toward the improvement of the techniques of geological investigations on engineering works; to further among engineers an understanding of the relationship between geology and engineering and the practical usefulness of geology in engineering.

FIELDS OF OVERLAP IN GEOLOGY AND ENGINEERING.

It goes without saying that the engineering geologist avails himself of all the facilities of the various branches of geologic science, including such special fields as petrography, geochemistry, geophysics, such special tools as X-ray diffraction and differential thermal analyses, the specialized contributions of groundwater hydrology, aerial photography and photo interpretations and the like—these are the tools he may use to elucidate fully the geological facts that bear on engineering problems.

Certain other fields, however, although they have distinct geological aspects and implications, are little known to geologists and seldom entered by geologists, except by force of necessity in connection with actual work on an engineering job. For instance, the fields of soil mechanics, concrete and concrete aggregate, and construction materials in general have been developed primarily by engineers and with insufficient awareness of the extent to which geology can contribute helpfully. We do not mean to deprecate the economic geologist engaged in the study of nonmetallic mineral deposits but merely to emphasize that few geologists have interested themselves sufficiently in the intricate considerations of testing, selection and use of such materials for specific engineering purposes. The field of sedimentation is one of more obvious overlap between engineering and geology. Engineers and geologists have pursued their separate researches in this field, each very intensive but lamentably inde-

pendent of each other—the geologist emphasizing the mineralogic aspects of sedimentation and viewing sedimentation as the complement of erosion, the engineer emphasizing the mechanical and hydraulic principles governing the transportation and deposition of sediments.

The role of the engineering geologist in these fields is discussed more specifically below.

Soil Mechanics.—Soil mechanics deals with the properties of soils in terms of their engineering behavior, such as their stability or permeability in embankments, their capacity for consolidation and settlement; the degree to which they can be compacted for special purposes, the pressures which they may exert against a retaining wall. Soil mechanics must remain primarily an engineering field, first, because its procedures and objectives are primarily of an engineering nature; and second, because few geologists are equipped with the knowledge of mechanics and mathematics necessary for its mastery. Nevertheless, it is imperative that an engineering geologist participate in and strive to understand soil mechanics. He needs insight into the concepts of soil mechanics in order properly to understand and interpret landslides, foundation settlements, the relative suitabilities of different types of soils for different purposes, and like matters. The geologist can also contribute materially to the field of soil mechanics because many of the principles of soil behavior which are now appraised by empirical tests will be rationalized ultimately only through geological and mineralogical insight in the origin, alteration, composition, and character of soil constituents. It is becoming increasingly apparent that such geologic and mineralogic factors are basic to the different behaviors exhibited by different soils. It is not the attempt of this report to review the progress of research in soil mechanics; such review is being made currently and adequately through various committees of the engineering societies. It is simply our intent herein to stress the necessity for further participation by geologists in the deliberations in the soil mechanics field and to indicate that some progress is being made in that direction.

Concrete and Concrete Aggregate.—As in soil mechanics, the concepts of this field have been developed empirically by experience and observation of concrete structures in service, and by intensive experimentation and research conducted mainly by engineers and, until recently, almost exclusively from the engineering point of view.

It is gratifying to report that the applications of geology and petrography to concrete and concrete aggregates have become greatly expanded in the last few years with highly profitable results. The most conspicuous accomplishments in this respect have been performed by petrographers who have contributed outstandingly to the concepts of concrete technology through the adaptation of the petrographic methods of rock study to concrete and through their special knowledge of the constituent rocks and minerals. Similar progress can be noted in the field investigation of aggregate sources; there is an increasing and mutually beneficial cooperation between geologists and materials engineers in the search for aggregates and the subsequent detailed investigations. The new techniques of interpretation of aerial photographs in terms of the types of materials comprising a terrain have been applied with notable

success to the location of aggregate deposits and the method is currently undergoing rapid expansion. The acceptance of geologists and geology into the fields of concrete technology and aggregate investigations is illustrated by the strong emphasis to be placed on geology and petrography in a forthcoming symposium on concrete aggregates now in preparation by the American Society for Testing Materials.

Materials Engineering in General.—As in the field of concrete and concrete aggregate, gratifying progress is evident in the increasing participation of geologists in studies of natural construction materials in general. In this field the geologist's contributions come naturally: in field investigations the geologist contributes through his knowledge of origin of materials, their modes of deposition, their manners of weathering, and their characteristic land forms; in the testing of materials, the geologist contributes through his knowledge of their chemical composition and mineralogic character; in the final appraisal of the suitability of different materials he is able to apply the principles of decomposition and disintegration which are so important to the question of potential durability under the anticipated conditions of service; in the interpretation of service histories of materials and of completed structures comprising such materials he may contribute helpfully through his familiarity with the natural processes of decomposition and disintegration. Specific research is in progress on rock materials for building purposes or protective riprap; earth materials for embankments, canal linings or special purposes; and clays, either in foundations or for particular uses as in impervious membranes to prevent seepage or in grouting.

Sedimentation.—As mentioned previously, sedimentation differs from these other fields of overlap in that the subject has long been a subject of geological specialization, while engineers, preoccupied with their own and very different objectives, have pursued their independent studies with equal vigor. Great advances have been made by other groups, but the need of today, if the field of sedimentation is to be made fully useful in its application of engineering problems, is that the two branches of study combine and operate hereafter in stronger coordination. By a very simple extension, the subject of sedimentation may be carried into materials engineering because so many deposits of natural construction materials owe either their origin or their present character to some process of sedimentation; and the same may be said of sedimentary rock foundations. It is in recognition of this fact that there is now proposed by the National Research Council a symposium on applied sedimentation which will contain chapters treating in detail the application of sedimentation to various phases of engineering geology.

However, the most direct application of sedimentation to engineering problems lies in the study of silting of reservoirs. This subject involves a variety of factors, both geological and engineering, including the sources of sediments and the identification of materials from various possible sources, the grain-size of the sediments with relation to the water velocities involved, the measurements of the bedload and suspended-load of entrant streams, topographic considerations related to erosion and deposition, and many others. In this field, the Bureau of Reclamation is now formulating a comprehensive program with

the ultimate objective of developing the relationship within a watershed between the character of materials available for erosion, the topographic character of the basin, the amount of rainfall and the percentage of runoff, the hydrologic regime of the streams, the character of the clay constituents carried to the reservoir in suspension, the manner of deposition, and—most important from the engineering standpoint—the density of the deposited sediments in the reservoir. This program, when actuated, will enlist the cooperative services of civil engineers, hydrologists, and geologists. In other sedimentation studies, directed toward the problems in specific river valleys, the Bureau of Reclamation and the Corps of Engineers and other agencies are performing cooperative researches.

In each of these fields of overlap between geology and engineering, perhaps the most encouraging development lies in an increasing desire on the part of most engineers and geologists to cooperate in joint efforts toward the solution of these mutual problems, which can be solved only incompletely or qualitatively—in general terms—by the independent efforts of either one or the other.

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ORGANIZATIONAL ADVANCES.

An outstanding post-war development in engineering geology has been the establishment within the United States Geological Survey of a unit devoted exclusively to this field. The establishment of this unit was in part a natural extension into the field of civilian engineering of the advances made by the Survey's unit of Military Geology during the war. But in part it was an expression of a recognition that engineering geology had become an independent field of geological specialization, deserving representation in the national survey.

With the formal entry of the Geological Survey into engineering geology, there are now four strong Governmental organizations actively participating in this field—the Geological Survey, the Tennessee Valley Authority, the Corps of Engineers, and the Bureau of Reclamation. In each of these organizations activity in engineering geology has recently increased in pace with the increase in civil works since the end of the war. The Tennessee Valley Authority resumed an active construction program. The geological activities of the Corps of Engineers have expanded in response to their enlarged program of civil construction. The Bureau of Reclamation has organized its engineering geology to include, in addition to the working geologists (and geophysicists and groundwater hydrologists), elaborate facilities for petrography and related studies, soil mechanics, and the investigation of natural construction materials, all placed in intimate organizational relationship to related units and laboratories with specialized facilities for chemistry, hydraulics, materials engineering, structural analysis, model making, electronic measurement and others.

In addition to these Federal agencies, there has been a significant increase in the utilization of geology in engineering works and the employment of engineering geologists by the larger municipalities, by state geological surveys and other agencies, such as highway departments, engaged in civil construction.

The most notable recent development in engineering geology within the technical and scientific societies has been the organization of a Section on Engineering Geology within the Geological Society of America. This is the first and so far the only technical organization devoted exclusively to the interests of engineering geology. The first formal meeting was held at the annual meeting of the Geological Society in Ottawa in December 1947, and included, in addition, the presentation of technical papers covering a wide variety of subjects within the field, a round-table discussion in which the objectives and destination of the newly organized section were discussed. Two matters of interest to this committee were suggested as possible "projects" for the new organization: (1) the formulation of an annotated bibliography on engineering geology and (2) the assembly of "case histories" of actual experiences in engineering geology to be used as teaching aids. Committees are to be appointed to consider these undertakings.

The Pan-American Institute of Mining Engineering and Geology at their second congress, in Brazil in October 1946, took a similar step by approving a recommendation made through the United States Delegation that engineering geology be embraced as a field of interest at the Institute's future congresses.

In Canada the applications of geology to engineering, and related research, are being rapidly accelerated by the National Research Council of Canada, especially through the efforts of R. F. Legget, Chairman of the Division of Building Research, who is sponsoring the applications of geology to a variety of engineering fields, with special emphasis upon the relationships between soil mechanics and geology, and upon the special peripheral fields of permafrost and muskeg. In the United States, the Geological Survey and the Corps of Engineers are also active in the latter two fields.

An important work of interest to this committee was recently begun through the formation in California of an Advisory Committee on Engineering Seismology to the United States Coast and Geodetic Survey. The objective of this subcommittee is to close the gap now existing between engineering and seismology so that accumulated seismologic data may be utilized more usefully in engineering. The scope of this Advisory Committee is indicated by the titles of the following subcommittees: Subcommittee for the Establishment of an Earthquake Research Institute; Subcommittee for Appraisal of Instrumental Progress; Subcommittee for the Collection of Engineering Information; Subcommittee on Publications and Library.

It is in line with the above comments to mention also the accelerated interest being shown by universities and colleges in the introduction of courses and research facilities in engineering geology. At the risk of slighting, through omission, other institutions deserving equal credit in this regard, we wish to mention the efforts being made at Washington University to establish a curriculum in engineering geology and to assemble specialized facilities in petrography, geophysics, sedimentation, X-ray, spectroscopic and thermal analysis, and the like, designed for research in this and other fields, as well as for course instruction.

SUMMARY OF CURRENT RESEARCH.

The following summary tabulation comprises the items of research supplied by various contributors to this report. The list is obviously incomplete but will serve to indicate the fields and breadth of research in engineering geology either in progress, recently completed, or contemplated for the immediate future.

Construction Materials.—Techniques of petrography are being applied extensively toward the formulation of a routine procedure of analysis of concrete aggregate. Research in progress aims to correlate the properties of aggregates with those of concrete, with particular reference to the mechanisms of alkali-aggregate reaction, the rocks susceptible to this reaction, and quick tests for potential reactivity of aggregates. Pozzolanic materials are the subject of intensive research to determine what natural materials are good pozzolans or can be made so by proper beneficiation and what pozzolans are most effective in retardation of alkali-aggregate reaction. Concrete is under study by petrographic methods to correlate its internal properties with its constituents and with its behavior in service. The petrography of cement clinker will be further correlated with the properties of cement by the application of these and related methods.

Extensive experimentation is being made on the use of power augers in lieu of test pits and in the use of aerial photographs to aid in locating the various types of materials that may be required. Geology and soil mechanics are being related from the standpoint of mineralogy, improved sampling and more realistic testing (see also *Clays* and *Durability and Breakdown,* below).

Site Investigation.—Experimentation in drilling methods and equipment is in progress for improvement of drilling equipment, especially the standardization of core barrels larger than nx. Experimentation also is in progress on a system of rotary-percussion drilling to obtain continuous samples on unconsolidated materials to depths of several hundred feet, and on the improvement of Denison and other types of undisturbed sampling equipment. Geophysical studies are being pushed toward their better application to site investigation; comparisons have been made between resistivity and seismic data in explorations of buried glacial gorges; experiments in progress will test the application of the gravimeter to the determination of density in place of unconsolidated foundation materials. The interpretation of aerial photographs for the determination of geological features at structure sites is being used and improved. Experiments are contemplated on electrical logging of drill holes.

Groundwater.—Research is in progress on the measurement of seepage losses in canals, on methods of drainage of water-logged lands, on the interpretation of groundwater studies in terms of damsite or reservoir leakage, on the effect of consolidation of sedimentary materials on permeability, on the development of improved equipment for groundwater measurements in the field, on the applications of electrical anology for the determination of constants to be used in field testing, and on the problem of turbulent flow through "open work" gravel.

Sedimentation and Related Fields.—Studies are in progress on the correlation of sediments in streams and the source rocks in river basins, on the mechanism of deposition of "open work" gravels, on the mechanisms and deposition of the clay fillings of the voids in gravels, on the applications of principles of sedimentation to the search for and properties of construction materials, and on the mechanism of silt transportation and deposition and silt measurement.

Foundation Treatment.—Studies are being made on vibratory compaction of unconsolidated materials in place, including the method of "vibroflotation" by which granular materials may be compacted at considerable depth. Studies are being made of the relationship between permeability and grout "take" in jointed and fractured rocks and on field tests, including geophysical methods, for determining the effectiveness of grouting.

Physical, Structural and Stratigraphic.—Landslides are under study in various localities with a view to determining and correlating their physical form, their constituent materials, and the "laboratory" properties of the constituent materials (angle of internal friction, cohesion, saturation, pore pressure). The rate of retreat of cliffs is being studied in the Northwest and the relationship between the repeated stratigraphic sequences in geotherms is being correlated with the problems involved in engineering works in Pennsylvania.

Clays.—Studies in progress are directed toward the more precise identification of clays, the correlation of their mineralogic character with their physical behavior (in both field and laboratory), and on the measurement of the magnitude of swell and swelling pressure developed by certain clays (including field tests on trial structures). Experiments are being made in the selection and use of clays for special purposes such as impervious membrane to prevent seepage or for grouting.

Durability and Breakdown of Rocks.—Research in progress will correlate the size, volume, and continuity of pores in rocks and concrete with resistance to freezing and thawing breakdown. The rate of solution of limestone is being studied with special reference to the effect of "chemical purity," the mechanism and rate of weathering and decay of arenaceous and siliceous rocks are being investigated.

Strength and Related Characteristics of Rocks.—The strength of rocks under conditions of triaxial loading is being investigated in connection with structure site investigations. Experiments in the utilization of the "ring test" for determinations of tensile and cohesive strength are being performed, particularly with a view to establishing techniques for testing nx cores in lieu of 5- or 6-inch cores. Static field tests for determining bearing strength and modulus elasticity are being correlated with parallel tests measuring wave velocity by geophysical means. Important studies have been made toward the measurement of residual stresses in rocks and a technique has been devised and successfully tested in the field for measuring such residual stress in tunnel walls.

Models and Exhibits.—Experimentation is in progress for the improvement of diagrams, transparent and non-transparent models, and peg models; in the use of aerial photographs for demonstration or study of geological fea-

tures at engineering sites; and on the improvement of methods of representing drill hole, groundwater, and related data on drawings and standard forms.

Study continues in several different directions leading toward the improvement of mechanisms for translating geologic data into engineering terms and making geologic data more useful and pertinent to engineers engaged in design and construction, especially through the mechanism of special work sheets, progress exhibits, and the like.

CONCLUSION.

Interest and activity in engineering geology is accelerating rapidly; it is rapidly becoming accepted generally as an independent and formalized field of geologic specialization; and a very large number of organizations and individuals are engaged in or contemplate research in engineering geology. As a consequence, research data are accumulating rapidly. For these reasons, we hold the opinion that it is unnecessary for any single group such as this committee to undertake or underwrite research. We believe, rather, that the committee can best serve the interests of engineering geology and the geological profession generally by maintaining a more or less continuous inventory of the applicable research contemplated or in progress, by preparing periodic summaries and appraisals of current research accomplishments and of the current orientation of research objectives, so that the various individual efforts may be more quickly synthesized and more readily coordinated.

WASHINGTON, D. C.,
March 8, 1948.

REVIEWS

Mapa de los Yacimientos Minerales de Bolivia con una Memoria Explicativa (Map of the Mineral Deposits of Bolivia with Explanatory Notes). By FEDERICO AHLFELD. Dirección General de Minas y Petróleo, Ministerio de Economía Nacional, La Paz, Bolvia, 1946.

The map of Bolivia is on the scale of 1:1,000,000, and the accompanying text comprises 19 pages. Condensed within this space is an enormous amount of information about the mineral production and mining industry of Bolivia.

The map does not include the portion of Bolivia east of longitude 63°, which contains no developed mineral deposits, but includes enormous deposits of hematite near the Brazilian border south of Puerto Suárez. The map shows the locations of all known Bolivian mineral deposits. Every square degree of latitude and longitude is numbered and divided into four quarters designated by letters. The text lists the districts by substances, indicating the more important producers and long idle mines by symbols, and gives their map location. Those who have tried to find the locations of the less known Bolivian mining districts and mines on hitherto available maps will fully appreciate this map.

In addition to providing a good planimetric map of Bolivia, showing the locations of the mineral deposits, the map shows the boundaries of the sub-Andine petroleum zone in the east and the tin zone of the Cordillera Oriental and eastern edge of the Altiplano, and the areas underlain by Tertiary granitic rocks, the Tertiary dacitic plugs, and the areas covered by late Tertiary volcanic lavas and tuffs.

Supplementing the map with a comprehensive yet condensed description of the distribution of the mineral deposits and a very informing summary of the mineral production of Bolivia are 9 pages of text.

Ahlfeld describes five geographic zones with a general trend west of north, parallel to the physiographic and geologic features of Bolivia. These zones from east to west are:

1. The petroliferous zone on the east flank of the Andes.
2. A zone further within the eastern Andean ranges that is poor in mineral deposits.
3. The stanniferous zone, related to the Tertiary intrusives, comprising the western part of the Cordillera Oriental, and including most of the metalliferous deposits. All of the tin, tungsten, bismuth, and antimony deposits, and a large part of the gold, silver, lead and zinc deposits are in this zone.
4. The Altiplano, in which the deposits are also of Tertiary age, and where are located most of the copper deposits and some of the lead, zinc, and silver deposits.
5. The Cordillera Occidental with sulphur, borates, and other evaporites of Quaternary age.

He gives an interesting analysis of the mineral production and trend of the Bolivian mining industry. The stanniferous zone yields 88 per cent to 94 per cent of the mineral exports in terms of value, and tin constitutes 72.8 per cent of the total. He believes his 1938 estimate of known tin reserves of 500,000 tons of tin

still holds, even though the subsequent exports amounted to 296,000 tons, through new developments, but points out that there has been a progressive decrease in tenor of the ores mined which now scarcely averages 2 per cent, and which is as low as 1 per cent or even less in some mines. In addition he estimates reserves of now sub-marginal ores with a tin content of at least 500,000 tons.

No definite estimate is presented of tungsten reserves. Since Ahlfeld's estimate of 25,000 tons of WO_3 in 1941, a great deal of tungsten has been produced, reaching a record peak of 4,761 tons WO_3 in 1944. However, he regards the reserves as still substantial, and predicts that under equally favorable market conditions the 1944 peak can be again achieved.

The only other tonnage estimate of reserves is for the Matilde zinc deposit which has 3,000,000 tons of ore containing 18.6 per cent zinc, 2.5 per cent lead, and 0.5 per cent copper. He considers Bolivia very rich in zinc deposits, but the only zinc producer now is the Pulacayo mine.

The areal distribution of the different kinds of mineral deposits is described briefly.

The larger metal mines are controlled by three groups of owners—the Patiño group, the Hochschild group, and the Aramayo group—and the mines under the control of each group are listed. In 1945, these groups controlled the production of 79.9 per cent of the tin, 54.4 per cent of the tungsten, and 93.4 per cent of the silver. The participation of the groups in the 1945 production was for tin—Patiño 45.2 per cent, Hochschild 27.7 per cent, Aramayo 7 per cent; for tungsten—Aramayo 45 per cent, Hochschild 5 per cent, Patiño 4.5 per cent; for silver—Hochschild 63 per cent, Aramayo 34.5 per cent.

The Bolivian metal mines are divided into three groups with respect to the size of their production—large, medium and small. The large mines are those of the three above groups. There is also a list of the medium size mines, mines that produce at least 7 tons of tin or 10 tons of tungsten monthly. The large mines number 36, of which 7 were idle in 1945, and 1 in the developmental stage. The medium size mines number 31, of which 3 were idle in 1945. These mines in 1944 produced 11.6 per cent of the tin, 21 per cent of the tungsten, and 34 per cent of the antimony. The small mines, which sell their production to the Banco Minero de Bolivia, produced in 1944, 6.7 per cent of the tin, 21 per cent of the tungsten, and 34 per cent of the antimony.

In 1943 the number of operating mines in Bolivia was 1176, among which were 616 tin mines, 240 tungsten mines, 166 antimony mines, and 26 copper mines. These four metals account for 1048 of the mines.

In his work on the Mineral Deposits of Bolivia published in 1941, Ahlfeld gave the metal production since 1900. These production figures are brought up to include the first half of 1946. The World War II peaks were lead, zinc and copper in 1941, tin and silver in 1942, antimony in 1943, and tungsten in 1944.

JOSEPH T. SINGEWALD, JR.

THE JOHNS HOPKINS UNIVERSITY,
BALTIMORE, MD.,
March 12, 1948.

Glacial Geology and the Pleistocene Epoch. By RICHARD FOSTER FLINT. Pp. 589; figs. 88; pls. 6 folding; references 40 pp. John Wiley & Sons, New York, 1947. Price, $6.00.

This much needed book is the only up-to-date volume that covers our present knowledge of Glaciology and the Ice Age. It not only admirably sums up existing

information but also presents several new concepts and points out new fields for research.

Some of the chapter headings best give an idea of the broad scope of the contents: Roots of Basic Concepts; Glacier Ice and Motion; Regimen of Glaciers; Form and Distribution of Existing Glaciers; Glacial Erosion and Transport; Glacial Landscapes; Glacial Drift; Expansion and Shrinkage; Glacial Drainage and Deposits; Glacial Stratigraphy; Glaciation of North America; Former Glaciers of Europe; Glaciation Outside of North America and Europe; Pleistocene Chronology; Changes in Level of Land and Sea; Glacial and Interglacial Climates; Subsequent Climates; Causes of Climatic Fluctuations; The Fossil Record; References (850 titles).

These broad chapters, it may be seen, cover the entire field of glaciation and the Pleistocene Epoch, including climate and crustal warping. In the chapter on the "Causes of Climatic Fluctuations" the author considers the seven items of basic data and considers that fluctuation in solar energy could cause glaciation at certain times of coincidence of uplift of highlands (Solar-Topographic Hypothesis).

The book is delightfully written, is well but sparsely illustrated, and is an outstanding contribution to glacial and Pleistocene literature and has an appeal not only to the glacial geologist but to geographers, archeologists, ecologists and everyone with a scientific interest in the great events of the ice age. It is comprehensive and must be considered the outstanding authority on this subject.

Seventy-five Years of Progress in the Mineral Industry. 75th Anniversary Volume of the American Institute of Mining and Metallurgical Engineers. Edited by A. B. PARSONS. Pp. 817; figs. and photographs. Amer. Inst. Min. and Met. Engrs., New York, 1947 (1948).

This long awaited volume brings together the outstanding special papers and lectures arranged for the 75th Anniversary of the Institute held in New York, March, 1947, participated in by 3,000 people and attended by 69 official representations from 20 countries. The session was a world conference on Mineral Resources dealing with resources, economics, and technology. Here are the subjects covered: Introduction, by Louis S. Cates; Seventy-five Years of Progress, with articles on Mining Geology by L. C. Graton, Metal Mining by Lucien Eaton, Ore Dressing by Arthur F. Taggart, Smelting and Leaching by Frederick Laist, Iron and Steel by C. D. King, Nonferrous Metallurgy by W. N. Peirce, Bituminous Coal Mining by H. N. Eavenson, Anthracite Industry by Cadwallader Evans, Jr., Chairman, Petroleum by E. L. DeGolyer, Nonmetallics by Oliver Bowles, Mineral Production by Elmer W. Pehrson, Mineral Industry Education by T. T. Read.

This 75 Years of Progress is followed by a History of the Institute by A. B. Parsons, Officers from 1871 to 1947, and the Proceedings of the Conference by the following distinguished authorities: Seventy-five Years of Achievement by the A. I. M. E. in the Mineral Industry by Cornelius F. Kelley, Mineral Position of the United States by J. A. Krug, Iron Ore and the Steel Industry by Charles M. White, International Aspects of the Petroleum Industry by Sir William Fraser, Copper, Lead and Zinc Mining in the Future by Clinton H. Crane, The Future of Gold in World Economy by P. M. Anderson, Tariffs, Cartels, and the Mineral Industry by Willard L. Thorp, South American Minerals in the Future World Economy by Pedro Beltrán, World Coal Resources by C. A. Carlow, The Philosophy of International Atomic Energy Control by John M. Hancock, The Role of the Engineer in the Development of Atomic Energy by P. C. Keith, Application of Atomic

Energy to Industry by H. A. Winne and B. R. Prentice, Petroleum and Natural Gas, Uses and Possible Replacements by R. E. Wilson and J. K. Roberts, Metals and Alloys of the Future by Zay Jeffries, Techniques of Mineral Exploitation of the Future by Louis S. Cates and Howland Bancroft, American Mining Enterprise in Foreign Countries by Spruille Braden.

This volume brings together a summing up of advances in the mineral industry during the period of great industrial development in the United States and in the world. The titles listed above speak for themselves and indicate the authoritative capacities of the authors and the broad coverage of the subject matter. It is a volume that will stand as a worthy companion to the other great special volumes brought out by the Institute and it is one that every person interested in the mineral industry will wish to own and to refer to continuously.

ALAN M. BATEMAN.

BOOK RECEIVED.

ALAN T. BRODERICK.

Riqueza Minera y Yacimientos Minerales de Mexico (Mineral Deposits of Mexico). J. GONZÁLEZ R. Pp. 446; maps 15; numerous tables. Monografía del Banco de Mexico, S. A. Mexico, D. F., 1947. *Mineral-by-mineral listing of 47 metallic and non-metallic (except oil) mineral products of Mexico. Production, reserves, geology of more important deposits. Colored geologic map of Mexico, scale 1:6,000,000.*

Boletín de la Escuela Nacional de Ingenieros (Bulletin of the National School of Engineers). Pp. 103; figs. 3. Tomo XX, Serie III. Lima, Peru, 1947. *Three articles including one on the etymology of mineralogic terms, one on small copper prospects south and east of Lima.*

An Outline of the Geological History of Southern Rhodesia. A. M. MACGREGOR. Pp. 73; table 1; map 1. S. Rhodesia Geol. Survey Bull. 38. Salisbury, 1947. *Report accompanies 30″ × 34″ colored geologic map, scale 1:1,000,000.*

Glass Sands of an Area Near Pretoria. L. MEINTJES AND H. J. NEL. Pp. 30; figs. 4; pls. 6. Union S. Africa Dept. Mines Geol. Series Bull. 17. Pretoria, 1947. *Large deposits of uncertain origin which yield good grade glass sands after beneficiation.*

Guide to the Geology of Central Colorado. Vol. 43, no. 2, Quarterly of the Colorado School of Mines. Pp. 176; figs. 38; pls. 14. Golden, Colo. Price, $3.00. This issue was published as the guidebook for the three field trips of the 33rd annual meeting of the American Association of Petroleum Geologists in Denver, April 26 to 29. *Principal features of the areas, road logs for the trips, geology of the eastern flank of the Front Range of Colorado; Kokomo, Gilman, and Leadville mining districts; Climax molybdenite deposit; oil-shale deposits in vicinity of naval oil-shale reserve, Garfield county; oil-shale demonstration plant at Rifle; and the geology of South Park.*

Les Traces de Glaciation et les Périodes Climatiques Glaciaires au Katanga et en Afrique Australe (The traces of Glaciation and the Glacial Periods of Katanga and Southern Africa). MAURICE ROBERT. Pp. 14. Comité Spécial du Katanga, op. 13, Brussels, 1947. *In Katanga traces of 5 glacial periods, A–E; most important, B, between Kundelungu and schisto-dolomitic*

systems, glacial cap of 150,000 km²; others seem local glaciation. Interior Southern Africa, one big glacial period, tillites of Pretoria series and "grikwatown" series; cold period of Witwatersrand, secondary. Western S. Africa, two important glacial periods, "Numees tillite" and "Chuos tillite" much older. All these glacial periods interrelated, but correlation of Transvaal and Nama systems now put in doubt.

Le Système de la Bushimaie au Katanga (The Bushimaie System in Katanga). L. CAHEN AND G. MORTELMANS. Pp. 38; figs. 12. Comité Spécial du Katanga, op. 14, Brussels, 1947. *The Bushimaie System occurs in Katanga and in the Kasai. Upper series, calcaro-dolomitic, more than 200 m thick, has same composition in Kasai and Katanga. Lower series, very reduced in Kasai (42 m at Bushimaie), more varied and important in Katanga (1,800 to 2,000 m thick) with arkosic and conglomeratic facies. Bushimaie System of Southern Katanga is equivalent to the Roan System.*

The Classification and Origin of Plateaux with Special Reference to India and the Adjacent Countries. H. L. CHHIBBER. Pp. 12. Nat. Geog. Soc. India Bull. 8, Benares, 1948.

Origin of Granite (Conference at Meeting of The Geological Society of America held in Ottawa, Canada, December 30, 1947). JAMES GILLULY, CHAIRMAN, PAPERS BY H. H. READ, A. F. BUDDINGTON, F. F. GROUT, G. E. GOODSPEED, N. L. BOWEN; DISCUSSION BY 26 AUTHORS. Pp. 139; pls. 12; figs. 5; tbl. 1. Geol. Soc. America Mem. 28. New York, 1948. Price, $1.80.

State Geological Survey of Kansas—University of Kansas Publications.

Bull. 65. Geology and Ground-Water Resources of Kiowa County, Kansas. B. F. LATTA. Pp. 151; pls. 11; figs. 10; tbls. 9. Lawrence, 1948.

Bull. 67. Kansas Clay, Dakota Formation. N. PLUMMER AND J. F. ROMARY. Pp. 241; pls. 7; figs. 17; tbls. 27. Lawrence, 1947. *1/3 white to buff-firing, 2/3 dark buff to red-firing. 150 to 400 billion tons estimated.*

Bull. 69. Geology and Ground-Water Resources of Seward County, Kansas. F. E. BYRNE AND T. G. MCLAUGHLIN. Pp. 140; pls. 12; figs. 10; tbls. 10. Lawrence, 1948.

U. S. Department of the Interior—Bureau of Mines.

Rept. Inv. 4205. Stalion-Curnel Fluorspar Prospect, Crittenden County, Ky. R. C. HICKMAN. Pp. 4; figs. 2. Washington, 1948. *Traces of fluorite in 5 drill holes, no production.*

Rept. Inv. 4207. Margerum Bauxite District, Colbert County, Ala. D. M. COULTER. Pp. 10; figs. 3; tbl. 1. Washington, 1948. *Bauxitized lenses of kaolin in the Tuscaloosa. Clay derived by erosion from Mississippian fms. 12 deposits total 187,000 tons 30–50% Al_2O_3.*

Rept. Inv. 4210. Black Rock Tungsten Deposit, Mono County, Calif. L. W. DUPUY. Pp. 11; figs. 10. Washington, 1948. *Scheelite in tactite. Reserves apparently small, not given. Interesting account of bulldozer trenching on slopes up to 28°.*

Rutgers University—Bureau of Mineral Research.

Bull. 1. Some New Jersey Glass Sands. A. S. WILKERSON AND J. E. COMEFORO. Pp. 156; figs. 2; tbls. 5; pl. 1. New Brunswick, 1948. *Field relations, mineral and chemical composition, results of beneficiation tests on 24 silica sand samples from Cretaceous to present deposits in N. J. 19 found amenable through treatment for use as glass sand.*

Inf. Circ. 2. Heavy Mineral Tailings from New Jersey Glass Sands. J. H. C. MARTENS. Pp. 10; tbls. 4. New Brunswick, 1948. *Possible minor source of Ti, Zr.*

Publications of the Instituto Geológico y Minero de España (Geological and Mining Institute of Spain). Madrid, 1941 to 1946.

La Interpretación Geológica de las Mediciones Geofísicas Aplicadas a la Prospección (The Geological Interpretation of Geophysical Measurements Applied to Prospecting). Vol. II. J. G. SIÑERIZ. Pp. 673; pls. 25; numerous tables. *Results of geophysical (magnetic, radioactive, electric, seismic) investigation of geologic problems in Spain.*

Bulletins.

Each of the following bulletins consists of several units, often not related to each other, on geological subjects. They are illustrated by numerous photos, figures, colored maps and sections.

Vol. 55 (15th of the 3rd series). Pp. 572. *Contains 8 articles, including one on the mineralography of pyrite, chalcopyrite and sphalerite at Río Tinto. Others on tectonics, paleontology, stratigraphy, hydrology and metallurgy.*

Vol. 56 (16th of the 3rd series). Pp. 649. *Contains 7 bulletins on coal genesis, stratigraphy, paleontology, flotation and hydrology.*

Vol. 57 (17th of the 3rd series). Part I. Pp. 362. *Structural geology, stratigraphy, paleontology of the area south of Valencia and north of Alicante, tectonics and mineral deposits of the Ebro Basin.* **Part II. Estudio Geológico del Sur de la Provincia de Valencia y Norte de la de Alicante.** B. DARDER PERICÁS. Pp. 470. *Stratigraphy, paleontology and structure of this area of Mesozoic and Cenozoic rocks.*

Vol. 58 (18th of the 3rd series). Pp. 519. *6 separate papers, including one on many copper prospects and mines in the Río Tinto area. Author proposes part sulphide injection, part hydrothermal origin. Microphotos, geol. maps.*

Vol. 59 (19th of the 3rd series). Pp. 364. *5 papers on Carboniferous stratigraphy and paleontology. Tectonics, study of the intrusive and metamorphic rocks of the Mataró sheet.*

Notes and Communications.

Periodic bulletins containing 10–14 independent papers on geologic subjects. Illustrated by photos, colored maps and sections.

No. 12. Pp. 179. *10 papers.*

No. 13. Pp. 322. *12 separate articles. Paleontology, 7; mineralogy 1 (cause of colors in tourmaline); stratigraphy and structure 3; hydrology 1.*

No. 14. Pp. 287. *8 separate articles. Orography, 1; paleontology, 3; stratigraphy and structure, 2; hydrology, 2.*

No. 15. Pp. 267. *Series of publications relating to general and economic geology of Spain.*

No. 16. Pp 381. *14 papers including articles on the problems of the genesis of the Rio Tinto type pyrite masses (19 pages), two unannotated chronologic bibliographies on tin and mercury in Spain.*

Australia Department of Supply and Shipping—Mineral Resources Survey. Canberra, 1945–1946.

Each of the following summary reports contains 15 to 45 pages of geologic and economic data on its product(s), including maps, figures, tables and references.

No. 1. Zirconium. *Bedded deposits of zircon, rutile and ilmenite in sands between tides and above, along former strand lines.*

No. 2. Titanium, (Rutile and ilmenite)—*Beach deposits, with zircon;* **No. 3. Antimony; No. 4. Mica; No. 5. Graphite; No. 6. Fluorite and Cryolite**—*Latter imported or synthesized;* **No. 8. Molybdenum; No. 9. Bismuth; No. 11. Magnesium; No. 12. Diatomite; No. 13. Barium; No. 14. Feldspar (including Cornish stone); No. 17. Asbestos; No. 18. Beryllium; No. 19. Tantalum and Columbium; No. 20. Mercury; No. 22. Arsenic; No. 24. Pigment Minerals; No. 25. Lithium; No. 26. Sillimanite, Kyanite, Etc.; No. 27. Aluminium and Bauxite; No. 30. Bentonite and Fuller's Earth.**

SCIENTIFIC NOTES AND NEWS

The American Association of Petroleum Geologists held its 33rd annual meeting along with the Society of Economic Paleontologists and Mineralogists and the Society of Exploration Geophysicists in Denver, April 26 to 29. The meetings began April 26 with addresses by Senator Antonio J. Bermudez, director of Petróleos Mexicanos, on "Mexican Oil" and V. F. Perry, of the U. S. Bureau of Mines, on "Prospects of Conversion of Western Coals to Synthetic Liquid Fuel." The following three days included a group of technical sessions. Among the papers presented was one by J. T. Duce and Max Steinecke, vice-president and chief geologist of the Arabian-American Oil Company, on "Oil in the Middle East" with a film showing life in the Middle East. Three field trips took place; one on April 26 to the foothills of the Front Range; another from Denver through Colorado Springs to Canyon City and return; the last one on April 30 included Precambrian to Cretaceous formations, the oil-shale demonstration near Rifle and return to Denver.

F. M. MURPHY, formerly geologist with the Union Pacific Railroad Company in Los Angeles, has moved to Las Vegas, Nevada, to engage in mining and geological consulting work.

FORBES S. ROBERTSON, of Rolla, Missouri, has joined the faculty of Montana School of Mines and will teach petrography, economic geology and related subjects during the school year, joining the Montana Bureau of Mines and Geology during the summer months after 1948.

RICHARD J. ANDERSON, economic geologist, has been appointed to the staff of Battelle Memorial Institute, Columbus, Ohio, where he will be engaged in studies on the economics of raw materials.

ALLAN M. SHORT, formerly mineral technologist for Missouri Pacific Lines, has announced that he is engaging in private practice as geologist and mineral technologist specializing in industrial raw materials.

LLOYD J. SEVERSON has been appointed assistant to general mining engineer by the Oliver Iron Mining Co., Duluth, Minn.

ARTHUR S. HECHT, consulting mining engineer of San Francisco, has been appointed consulting engineer for the Department of Commerce military government in Korea.

JOSEPH E. FOWELLS is employed as resident geologist by the Miami Copper Co., Miami, Ariz.

HENRY R. WARDWELL, formerly with the U. S. Vanadium Corporation, is working as geologist with the Magma Copper Co., Superior, Ariz.

HUGO H. BEIN resigned as engineer and geologist for the Best Mines Co., Downieville, Calif., to go to the Philippine Islands.

FRANK A. HERALD joined the staff of the Bureau of Economic Geology, University of Texas, Austin, on Jan. 1. He will act as editor and supervisor for a summary of the oil fields of Texas.

HEINRICH RIES is giving a series of lectures on Clays and Foundry Sands at the Department of Ceramics, Rutgers University, New Brunswick, N. J.

RAY E. MORGAN is head of the department of mining and geology at the West Virginia Institute of Technology, Montgomery, W. Va. He had been with the Mene Grande Oil Co. in Venezuela.

WILFORD S. WRIGHT is engaged in mining activities in Korea as an engineer for the U. S. Department of Commerce, Bureau of Mining. During the war Mr. Wright did exploratory work for the Bureau of Mines in Alaska.

ALEX L. DUTOIT, long Associate Editor of this JOURNAL, died in Capetown, South Africa, on February 25th.

B. S. BUTLER, head of the department of geology and mineralogy at the University of Arizona, will retire July 1 to be succeeded by MAXWELL N. SHORT.

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